LISTING BACKGROUND DOCUMENT
FOR
THE 1992-1996 PETROLEUM REFINING
LISTING DETERMINATION

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Prepared For:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Solid Waste
Characterization and Assessment Division
401 M Street, SW
Washington, DC 20460

Prepared By:

Science Applications International Corporation
Environmental and Health Sciences Group
1710 Goodridge Drive
McLean, VA 22102

INDUSTRIAL SOLID AND HAZARDOUS WASTE
CHARACTERIZATION SUPPORT CONTRACT

EPA Contract No. 68-W4-0042, WA No. 2
SAIC Project No. 01-0825-07-1964-006

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1.0 INTRODUCTION

1.1 BACKGROUND

The U.S. Environmental Protection Agency's (EPA's) Office of Solid Waste (OSW), as directed by Congress in the Hazardous and Solid Waste Amendments of 1984 to the Resource Conservation and Recovery Act (RCRA), has undertaken an investigation of the Petroleum Refining Industry. This investigation was also mandated by a 1994 consent decree resulting from litigation brought by the Environmental Defense Fund (EDF). The consent decree identifies 14 specific residuals for which the Agency must make listing determinations and an additional 15 residuals that the Agency must study. These 29 residuals, subsequently referred to as the Residuals of Concern (RCs), are listed in Table 1.1. As a result of the consent decree, the Agency embarked on a three-year project to determine whether these 29 RCs pose a threat to human health and the environment and to develop a basis for making such a determination. This background document presents the information collected to support the 14 listing determinations.

The Petroleum Refining Industry was previously studied by OSW in the 1980s. This original effort involved sampling and analysis of a number of residuals at 19 sites, distribution of a RCRA §3007 questionnaire to 180 refineries (characterizing the industry as of 1983), and, ultimately, a listing determination effort focused on wastewater treatment sludges, culminating in the promulgation of hazardous waste listings F037 and F038 (respectively, primary and secondary oil/water/solids separation sludges from petroleum refining).

As part of the Agency's current investigation of residuals from petroleum refining, the Agency conducted engineering site visits to 20 refineries to gain an understanding of the present state of the industry. These 20 refineries were randomly selected from the 185 refineries operating in the continental United States in 1992. Familiarization samples of various residuals were collected at 3 refineries to obtain data on the nature of the RCs and to identify potential problems with respect to future analysis. The Agency then conducted record sampling and analysis of the RCs. During the record sampling timeframe, an additional 6 facilities were randomly selected to increase sample availability. Approximately 100 record samples were collected and analyzed. Concurrently, the Agency developed, distributed and evaluated a census survey of the industry. Science Applications International Corporation (SAIC) (EPA Contract No. 68-W4-0042) has been contracted to assist EPA/OSW in the characterization and evaluation of these residuals.

Table 1.1. Petroleum Refining Residuals Identified in the EDF/EPA Consent Decree

Sludges\Sediments:

Clarified slurry oil sediments and filter solids from catalytic cracking (L) (CSO sludge)
Unleaded storage tank sediments (L)
Crude storage tank sediments (L)
Process sludge from sulfur complex and H_2S removal facilities (L) (sulfur complex sludge)
Sludge from HF alkylation (L)
Sludge from H_2SO_4 alkylation (L)
Desalting sludge from crude desalting (S)
Residual oil storage tank sludge (S)
Process sludge from residual upgrading (S)

Catalysts:

Catalyst from catalytic hydrotreating (L)
Catalyst from catalytic reforming (L)
Catalyst and fines from catalytic cracking (L) (FCC catalyst and FCC fines)
Catalyst from catalytic hydrorefining (L)
Catalyst from H_2SO_4 alkylation (L)
Catalyst from sulfur complex and H_2S removal facilities (L) (Claus and tail gas treating catalysts)
Catalyst from extraction/isomerization process (S)
Catalyst from catalytic hydrocracking (S)
Catalyst from polymerization (S)
Catalyst from HF alkylation (S)

Off-Spec Products:

Off-spec product and fines from thermal processes (L)
Off-spec product and fines from residual upgrading (S)
Off-spec product from sulfur complex and H_2S removal facilities (S)

Treating Clays:

Treating clay from clay filtering (S)
Treating clay from lube oil processing (S)
Treating clay from the extraction/isomerization process (S)
Treating clay from alkylation (S)

Miscellaneous Residuals:

Spent caustic from liquid treating (L)
Off-spec treating solution from sulfur complex and H_2S removal facilities (S)
Acid-soluble oil from HF alkylation (S)

L: Requires listing determination as per the EDF/EPA consent decree.
S: Requires study as per the EDF/EPA consent decree.

1.2 EXISTING PETROLEUM REFINING LISTINGS

As a result of past listing investigations, the Agency previously promulgated a series of listings that apply to the petroleum refining industry. These listings are associated primarily with the refinery wastewater treatment systems. The consent decree residuals, in contrast, are not wastewater treatment residuals, although some of the residuals of concern are typically managed in the refinery wastewater treatment plants. The existing listings are described below:

Hazardous Waste Listing	Listing Description	Date of Pub.
K048	Dissolved air flotation (DAF) float from the petroleum refining industry (T)	5/19/80
K049	Slop oil emulsion solids from the petroleum refining industry (T)	5/19/80
K050	Heat exchanger bundle cleaning sludge from the petroleum refining industry (T)	5/19/80
K051	API separator sludge from the petroleum refining industry (T)	5/19/80
K052	Tank bottoms (leaded) from the petroleum refining industry (T)	5/19/80
F037	Petroleum refinery primary oil/water/solids separation sludge - Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oily cooling wastewaters from petroleum refineries. Such sludges include, but are not limited to, those generated in: oil/water/solids separators; tanks and impoundments; ditches and other conveyances; sumps; and stormwater units receiving dry weather flow. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and K051 wastes are not included in this listing.	11/2/90

Hazardous Waste Listing	Listing Description	Date of Pub.
F038	Petroleum refinery secondary (emulsified) oil/water/solids separation sludge - Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, all sludges and floats generated in: induced air flotation (IAF) units, tanks and impoundments, and all sludges generated in DAF units. Sludges generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges and floats generated in aggressive biological treatment units as defined in §261.31(b)(2) (including sludges and floats generated in one or more additional units after wastewaters have been treated in aggressive biological treatment units) and F037, K048, and K051 wastes are not included in this listing.	11/2/90

Section 261.3(a)(2)(iv)(C) exempts K050 from the definition of hazardous waste when mixed with wastewater discharged under either section 402 or 307(b) of the Clean Water Act.

Section 261.4(a)(7) exempts spent sulfuric acid used to produce virgin sulfuric acid, unless it is accumulated speculatively as defined in §261.1(c). Spent sulfuric acid is one of the listing residuals of concern.

1.3 OTHER EPA REGULATORY PROGRAMS IMPACTING THE PETROLEUM REFINING INDUSTRY

Each of EPA's major program offices has long-standing regulatory controls tailored to the petroleum refining industry. Some of the more significant programs with some relevance to OSW's listing determinations include:

- The Clean Air Act's Benzene NESHAPs, designed to control benzene releases from process and waste management units.
- The Clean Air Act's National Ambient Air Quality Standards (NAAQS), which prescribe limits for SOx, CO, particulates, NOx, VOCs, and ozone.

- The Clean Air Act's NESHAPS for Petroleum Refineries (40 CFR Part 63 Subpart CC. August 18, 1995, 60 FR 43244, designed to control hazardous air pollutants (HAPs).

- Fuel specification rules established under the Clean Air Act which set the acceptable composition of gasoline and diesel fuel.

- The Clean Water Act sets specific technology-based limits and water quality-based standards for discharges to surface waters and POTWs.

- The Toxicity Characteristic, particularly for benzene, in combination with the F037/F038 sludge listings, has had a significant impact on the industry's wastewater treatment operations, forcing closure of many impoundments and redesign of tank-based treatment systems.

- The LDR Program, including the ongoing Phase III and IV development work.

2.0 INDUSTRY DESCRIPTION

2.1 PETROLEUM REFINING INDUSTRY PROFILE

In 1992, the U.S. petroleum refining industry consisted of 185 refineries owned by 91 corporations. Figure 2-1 illustrates the distribution of refineries across the country. Refineries can be classified in terms of size and complexity of operations. Forty-four percent of the refineries process less than 50,000 barrels per day of crude, while the 20 largest companies account for 56 percent of the nation's total refining capacity.

The simplest refineries use distillation to separate gasoline or lube oil fractions from crude, leaving the further refining of their residuum to other refineries or for use in asphalt. Approximately 18 percent of the U.S.'s refineries are these simple topping, asphalt, or lube oil refineries. More sophisticated refineries will have thermal and/or catalytic cracking capabilities, allowing them to extract a greater fraction of gasoline blending stocks from their crude. The largest refineries are often integrated with chemical plants, and utilize the full range of catalytic cracking, hydroprocessing, alkylation and thermal processes to optimize their crude utilization. Section 3.0 describes the major unit operations typically found in refining operations.

The refining industry has undergone significant restructuring over the past 15 years. While the total national refining capacity dropped 17 percent since 1980 to 15 million barrels per day, the number of refineries dropped 45 percent from 311 in 1980 to approximately 171 active in 1992. Refinery utilization rates over the 1980 to 1992 period rose from 75 percent to 90 percent. (API, 1993). Very few new refineries have been constructed in the past decade; the industry instead tends to focus on expansions of existing plants.

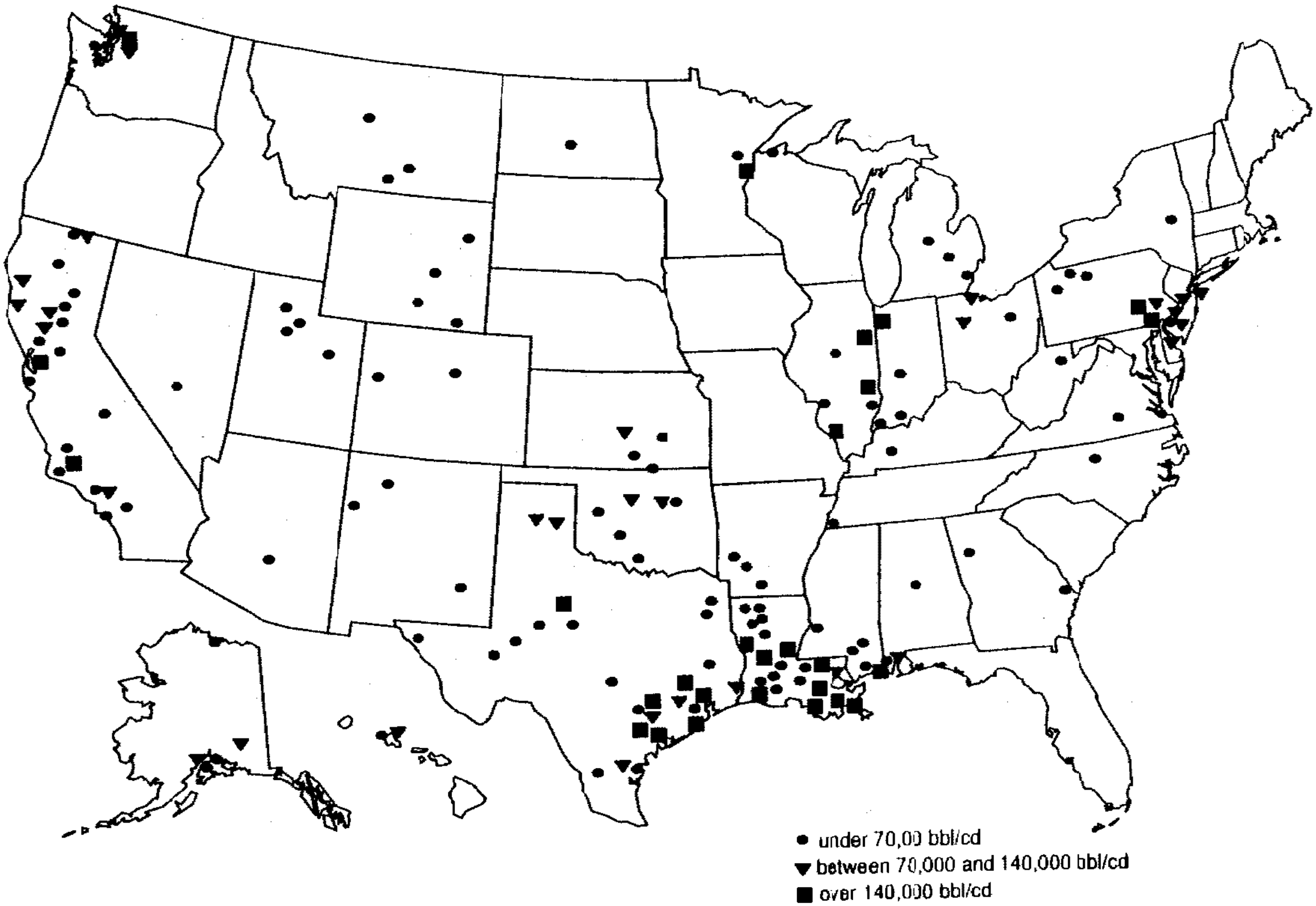
The facilities closed fended to be smaller, inefficient refineries. Larger existing facilities with capacities over 100,000 bbl/day have increased production to off-set the facility closings.

The data presented above indicates that the petroleum refining industry has been going through a consolidation, which has resulted in a large decrease in the number of refineries in the United States, but only a slight decrease in production. It is expected that this trend will continue, with refineries continuing to close, but expansions occurring at others, keeping the total refinery capacity in line with demand for refinery products.

In addition to restructuring, the industry is adding and changing production operations. Although atmospheric and vacuum distillation, catalytic cracking, and their associated treating and reforming operations will remain the primary refinery operations, new production operations continue to be added. These include coking and desulfurization processes.

Many of these process changes are being implemented as a result of two factors: (1) today's crudes tend to be heavier and contain higher levels of sulfur and metals, requiring process modifications, and (2) a series of important pollution control regulations have been implemented, including new gasoline reformulation rules designed to reduce the amount of volatile components in gasoline, and new regulations requiring low-sulfur diesel fuels. These heavier crudes and new rules are causing refineries to make process modifications to their catalytic cracker units, as well as installing additional sulfur removal hydrotreaters and unit processes to manufacture additives.

Figure 2.1. Geographical Distribution of U.S. Refineries



2.2 INDUSTRY STUDY

OSW's current listing determination for the petroleum refining industry has been underway since 1992 and can be characterized in terms of two major avenues for information collection: field work and survey evaluation. As part of the Agency's field work, engineering site visits, familiarization sampling, and record sampling were conducted. The survey effort included the development, distribution, and assessment of an extensive industry-wide RCRA §3007 survey. Each of these elements is described further below, reflecting the relative order in which these activities were conducted over the past three years.

2.2.1 Engineering Site Visits

EPA's field work activities were initiated with a series of engineering site visits. The primary purpose of these visits was to gather information about the 29 consent decree residuals and to identify appropriate sampling locations. After considering logistical and budgetary constraints, the Agency determined that it would conduct engineering site visits at 20 refineries prior to record sampling.

The Agency defined a site selection procedure that was used in selecting the 20 site visits from the population of 185 domestic refineries in the continental U.S.. The objectives of the selection procedure were:

- to ensure that the characterization data obtained from residuals at the 20 selected facilities could be used to make valid, meaningful statements about those residuals industry-wide.

- to give the Agency first-hand exposure to both large and small refineries.

- to be fair to all domestic refineries.

The Agency chose to select facilities randomly rather than purposefully. Although a randomly selected group of refineries may not offer as many sampling opportunities as a hand-picked group, the Agency favored random selection because it did not require subjective input, and also because it lends itself to statistical analysis, which is useful in making general statements about the population of residuals.

The Agency broke the industry into two strata based on atmospheric distillation capacity and made random selections from each stratum independently. The high-capacity stratum contains the top 30% of refineries, which together account for 70% of the refining industry's capacity. The stratification enables the Agency to weigh the selection toward the larger facilities on the basis that they produce larger volumes of residuals, and that they offer a larger number of residual streams per site visit. The Agency chose to select 12 of the 20 site visits, 60%, from the high-capacity stratum. The smaller facilities had a lower chance of being selected, but not as low as they would have if the likelihood of selection was based strictly on size. The selected facilities are presented in Table 2.1[1].

An engineering site visit report was developed for each of the trips; these are available in the CBI and non-CBI dockets, as appropriate. For the later site visits conducted in 1994 and 1995, the engineering site visit reports were combined with the analytical data reports prepared for each facility. The site visit reports included the following elements:

- Purpose of the site visit
- Refinery summary, including general information gathered during the site visit, as well as data gleaned from telephone conversations and reviews of EPA files, the refinery's process flow diagram, and expected residual availability
- A discussion of the processes used at the refinery generating the residuals of concern
- Source reduction and recycling techniques employed by the refinery
- A description of onsite residual management facilities
- A chronology of the site visit.

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[1] Upon initial contact with several of the randomly selected refineries, it was determined that they were inappropriate candidates for site visits because they had stopped operation and were not generating any residuals of interest to the Agency. Replacement facilities were then selected randomly from the same stratum.

The list of refineries slated for field investigations was expanded in June, 1994 to allow the Agency to fill out certain categories of samples that proved to be difficult to find in the field. The final list presented in Table 2.1 represents those refineries at which site visits actually occurred.

Table 2.1. Engineering Site Visit Facilities		
Refinery	Location	Initial Site Visit Date
Amoco Oil	Texas City, Texas	March 29, 1993
Arco	Ferndale, Washington	June 9, 1993
Ashland	Canton, Ohio	May 24, 1993
Ashland	Catlettsburg, Kentucky	March 22, 1993
BP Oil	Belle Chasse, Louisiana	May 3, 1993
BP Oil	Toledo, Ohio	May 26, 1993
Chevron (purchased by Clark) [1]	Port Arthur, Texas	August 31, 1994
Chevron [1]	Salt Lake City, Utah	February 21, 1995
Conoco [1]	Commerce City, Colorado	To be determined
Exxon	Billings, Montana	June 9, 1993
Koch	St. Paul, Minnesota	May 19, 1993
Little America	Evansville, Wyoming	June 8, 1993
Marathon	Garyville, Louisiana	April 22, 1993
Murphy	Superior, Wisconsin	May 17, 1993
Pennzoil	Shreveport, Louisiana	May 5, 1993
Phibro Energy [1]	Houston, Texas	April 20, 1995
Rock Island (purchased by Marathon)	Indianapolis, Indiana	April 26, 1993
Shell	Deer Park, Texas	March 31, 1993
Shell	Norco, Louisiana	April 20, 1993
Shell	Wood River, Illinois	May 28, 1993
Star Enterprise [1]	Convent, Louisiana	August 30, 1994
Star Enterprise [1]	Port Arthur, Texas	September 21, 1994
Sun	Philadelphia, Pennsylvania	May 12, 1993
Texaco	Anacortes, Washington	June 10, 1993
Total	Ardmore, Oklahoma	June 23, 1993
Young	Douglasville, Georgia	June 21, 1993

[1] Refinery selected to augment record sample availability.

2.2.2 RCRA §3007 Questionnaire

EPA developed an extensive questionnaire under the authority of §3007 of RCRA for distribution to the petroleum refining industry. A blank copy of the survey instrument is provided in Appendix A. The questionnaire was organized into the following areas:

- Corporate and facility information
- Crude oil and product information
- Facility process flow diagram
- Process units: general information
- Process units: flow diagrams and process descriptions
- Residual generation and management
- Residual and contaminated soil and debris characterization
- Residual management units: unit-specific characterization
- Unit-specific media characterization
- General facility characterization (focusing on exposure pathway characterization)
- Source reduction efforts
- Certification

The survey was distributed in August 1993 to all refineries identified as active in 1992 in the DOE Petroleum Supply Annual. Of the 185 surveys distributed, completed responses were obtained for 172 refineries. An additional 13 refineries notified EPA that they had stopped operations at some point in or after 1992 and thus were unable to complete the survey due to no staffing or inaccessible or unavailable data.

The completed surveys were reviewed by SAIC chemical engineers for completeness and then entered into a relational data base known as the 1992 Petroleum Refining Data Base (PRDB). The entries were subjected to a series of automated quality assurance programs to identify inappropriate entries and missing data links. An exhaustive engineering review of each facility's response was then conducted, resulting in follow-up letters to most of the industry seeking clarifications, corrections, and additional data where needed. The responses to the followup letters were entered into the database. A wide variety of additional quality assurance checks were run on the data, with added emphasis on the listing residuals, to ensure that the residuals of concern were characterized as completely and accurately as possible. Follow-up telephone interviews were conducted as necessary to address remaining data issues. After extensive review, the Agency believes that the data are reliable and represent the industry's current residual generation and management practices.

Table 2.2 describes the survey results for each of the listing residuals of concern, sorted by total volume generated in metric tons (MT).

Table 2.2. Listing Residuals Volume Statistics

Listing Residual Description	# of Reported Residuals	Total Volume (MT)
Catalyst from H2SO4 Alkylation	56	1,760,071
Spent Caustics from Liquid Treating	631	917,656
Off-Spec Product and Fines from Thermal Process	90	194,262
FCC Catalyst	179	124,061
FCC Fines	105	67,816
CSO Sediments	42	24,010
Crude Oil Tank Sediments	99	22,017
Catalyst from Hydrorefining	73	18,634
HF Alkylation Sludge	33	11,288
Sulfur Complex Sludge (other than Stretford)	268	8,520
Catalyst from Hydrotreating	184	5,640
Catalyst from Claus Unit	93	3,819
Unleaded Gasoline Tank Sediments	125	3,583
Catalyst from Reforming	104	3,613
Sulfuric Acid Alkylation Sludge	13	608
Tail Gas Treating Catalyst (SCOT®-like)	23	361

2.2.3 Familiarization Sampling

The early phases of the analytical phase of this listing determination consisted of the development of a Quality Assurance Project Plan (QAPjP) for sampling and analysis, followed by the collection and analysis of five "familiarization" samples. The purpose of collecting these samples was to assess the effectiveness of the methods identified in the QAPjP for the analysis of the actual residuals of concern. Due to the high hydrocarbon content of many of the RCs, there was concern at the outset of the project that analytical interferences would prevent the contracted laboratory from achieving adequate quantitation limits; familiarization analysis allowed the laboratories to experiment with the analytical methods and waste matrices and optimize operating procedures.

In addition, the first version of the QAPjP identified a list of target analytes that was derived from previous Agency efforts to characterize refinery residuals. These included the Delisting Program's list of analytes of concern for refinery residuals, the "Skinner List", an evaluation of compounds detected in the sampling and analysis program for listing refinery residuals in the 1980s, and the judgement of EPA and SAIC chemists who evaluated the process chemistry of the residuals of concern. During familiarization sample analysis, particular attention was paid to the tentatively identified compounds to determine whether they should be added to the target analyte list.

Samples of five listing residuals were collected for familiarization analysis: crude oil tank sediments, hydrotreating catalyst, sulfur complex sludge, H_2SO_4 alkylation catalyst, and spent caustic. One study residual, acid soluble oil, was analyzed under this program. The results of the familiarization effort essentially confirmed the techniques identified in the QAPjP and indicated that the laboratories generally would be able to achieve adequate quantitation of the target analytes. The familiarization and final QAPjPs are provided in docket to this proposed rulemaking.

2.2.4 Record Sampling

Upon completion of the familiarization sampling and analysis effort, the Agency initiated record sampling and analysis of the listing and study residuals. Given budgetary constraints, the Agency set a goal of collecting 4-6 samples of each of the listing residuals, and 2-4 samples of the study residuals for a total of 134 samples[2]. Table 2.3 shows the 103 samples that were actually collected. The numbers in the darkened boxes refer to Table 2.4 which lists each of the sample numbers, sample dates, facility names, and other information describing the residual samples.

The sampling team maintained monthly phone contact with the targeted refineries to maintain an optimized sampling schedule. Despite careful coordination with the refineries and best efforts to identify and collect all available samples, there were several categories for which the targeted minimum number of samples could not be collected:

- Three samples of unleaded gasoline tank sediments were collected. This residual is available only for a brief period during tank turnarounds, which may occur only every 10 years. In several cases, refineries informed EPA of planned tank turnarounds only to find no sediments upon opening the tanks for inspection. See Section 3.1.2.

- Three samples of hydrorefining catalyst were collected. As with the unleaded gasoline tank sediments, this residual is only generated on a periodic basis (e.g., every 3-5 years). Heroic efforts to locate additional samples were not expended because of the expected similarity between this residual and hydrotreating catalyst, for which 6 samples were successfully collected. As illustrated above in Table 2.2, the PRDB indicates that there were over twice the number of hydrotreater turnarounds (and catalyst generation events) as there were hydrorefiners.

- One sample of sulfuric acid alkylation sludge was collected. As is discussed further in Section 3.5.3, the Agency believes that this residual was

[2] The Agency determined that one listing residual, catalyst from sulfuric acid alkylation, would not be sampled due to the existing regulatory exemption for sulfuric acid destined for reclamation, and that one study residual, catalyst from HF alkylation, would not be sampled because the Agency believed it had been classified as a residual of concern inappropriately based on erroneous old data.

inappropriately misclassified as a listing residual due to the evaluation of inaccurate old data. This residual is not readily available, and was extremely difficult to find.

Each of the samples collected was analyzed for the total and TCLP concentrations of the target analytes identified in the QAPjP. In addition, certain residuals were tested for different characteristics based on the Agency's understanding of the residuals developed during the engineering site visits. Each sample was also analyzed for the ten most abundant nontarget volatile and the 20 most abundant nontarget semi-volatile organics in each sample. These tentatively identified compounds (TICs) were not subjected to QA/QC evaluation (e.g., MS/MSD analyses) and thus were considered tentative. The TIC results are available in the analytical data reports in the public docket to the proposed rule.

2.2.5 Split Samples Analyzed by API

The American Petroleum Institute (API) accompanied the EPA contractor (SAIC) on virtually all sampling trips and collected split samples of many of the record samples. API's analytical results for a number of the samples were made available to EPA for comparison purposes. In general, the Agency found that the API and EPA split sample analyses had very good agreement. Appendix B presents the Agency's comparison of the split sample results.

Table 2.3. Residuals Collected for Record Analysis

Exhibit 2. Impact of Potential Fall Sampling Opportunities on the Petroleum Refining Listing Determinations and Industry Study Sampling Effort

Sept. 21, 1995

Listing Residuals	Record Samples 1	2	3	4	5	6	Familiarization Samples 1
Crude oil tank sludge	33	67	73	53	89	91	F5
Unleaded gasoline tank sludge	34	42	65				
CSO sludge	14	49	72	88			
FCC catalyst and fines	1	12	13	26	27	28	
Catalyst from hydrotreating	6	11	55	83	94	69	F2
Catalyst from hydrorefining	21	36	85				
Catalyst from reforming	3	22	37	56	79	75	
Sulfuric acid alkylation sludge	46						
HF alkylation sludge	19	47	51	74	96		
Sulfur complex sludge	10	25	29	80	70		F3
Catalyst from sulfur complex	9	15	23	24	52	54	
Off-spec product & fines/thermal process	30	45	59	63	81	84	
Spent caustic	16	17	32	62	64	95	F1

Study Residuals	1	2	3	4	extra	Familiarization Samples 1
Residual oil tank sludge	41	92				
Desalting sludge	5	50	90	102		
Hydrocracking catalyst	4	43	87			
Catalyst from isomerization/extraction	39	48	71	97		
Treating clay from isomerization/extraction	68	98				
Catalyst from polymerization	35	66A	66B			
Treating clay, alkylation (HF and H2SO4)	20	76	86	99		
ASO	18	38	77	93		F4
Off-spec sulfur	2	8	40	100		
Spent amine solution	61	58	82	78		
Process sludge from residual upgrading	11					
Off-spec product, residual upgrading						
Treating clay from lube oil	60					
Treating clay from clay filtering	7	31	57	101		

Notes:
Sulfuric Acid Alkylation catalyst is not presented in this figure. One familiarization sample of sulfuric acid catalyst was captured and analyzed.
HF catalyst is constant boiling mixture (CBM) and is not shown in this figure.
ASO is polymer.

Table 2.4. Descriptions of Samp... Collected for Record Analysis

Petroleum Refining Listing Determinations and Industry Study — 21-Sep-95
Exhibit 2. List of Samples Captured to Date

Record Samples

Count	Residual Name	Sample Number	Sample Date	Notes	Refinery
1	FCC catalyst and fines	R2-FC-01	30-Sep-93	ESP Fines.	Shell, Wood River, Illinois
2	Off-spec sulfur	R2-SP-01	30-Sep-93	Taken from low spots on the unit.	Shell, Wood River, Illinois
3	Catalyst from reforming	R2-CR-01	01-Oct-93	Platinum catalyst.	Shell, Wood River, Illinois
4	Catalyst from hydrocracking	R2-CC-02	04-Oct-93	2nd stage, Ni/W.	Shell, Wood River, Illinois
5	Desalting sludge	R1-DS-01	26-Oct-93	Removed from vessel.	Marathon, Indianapolis
6	Catalyst from hydrotreating	R1-TC-01	26-Oct-93	Naphtha reformer pretreat, CoMo.	Marathon, Indianapolis
7	Treating clay	R1-CF-01	27-Oct-93	Kerosene.	Marathon, Indianapolis
8	Off-spec sulfur	R1-SP-01	27-Oct-93	From product tank.	Marathon, Indianapolis
9	Catalyst from sulfur complex	R1-SC-01	27-Oct-93	Al2O3.	Marathon, Indianapolis
10	Sulfur complex sludge	R1-ME-01	27-Oct-93	MEA reclaimer bottoms.	Marathon, Indianapolis
11	Process sludge from residual upgrading	R1-RU-01	27-Oct-93	ROSE butane surge tank sludge.	Marathon, Indianapolis
12	FCC catalyst and fines	R4-FC-01	16-Nov-93	Equilibrium cat. from hopper.	Little America, Evansville, Wy
13	FCC catalyst and fines	R4-FC-02	16-Nov-93	ESP fines. truck trailer comp.	Little America, Evansville, Wy
14	CSO sludge	R4-SO-01	16-Nov-93	Tank sludge from pad.	Little America, Evansville, Wy
15	Catalyst from sulfur complex	R4-SC-01	16-Nov-93	Claus unit alumina, super sack comp.	Little America, Evansville, Wy
16	Spent caustic	R3-LT-01	18-Nov-93	Tank samp. Cresylic, concentrated.	Exxon, Billings, Montana
17	Spent caustic	R3-LT-02	18-Nov-93	Tank samp. Sulfidic, concentrated.	Exxon, Billings, Montana
18	ASO	R3-AS-01	18-Nov-93	Non-neutralized, separator drum sample	Exxon, Billings, Montana
19	HF alkylation sludge	R3-HS-01	18-Nov-93	Not dewatered. Dredge from pit.	Exxon, Billings, Montana
20	Treating clay from alkylation	R3-CA-01	18-Nov-93	HF. Propane treater. Drum composite.	Exxon, Billings, Montana
21	Catalyst from hydrorefining	R5-TC-01	07-Feb-94	Heavy Gas Oil, CoMo	Marathon, Garyville, LA
22	Catalyst from reforming	R5-CR-01	07-Feb-94	CCR fines, Pt	Marathon, Garyville, LA
23	Catalyst from sulfur complex	R5-SC-01	07-Feb-94	Claus	Marathon, Garyville, LA
24	Catalyst from sulfur complex	R5-SC-02	07-Feb-94	Tail gas, CoMo	Marathon, Garyville, LA
25	Sulfur complex sludge	R5-ME-02,03	07-Feb-94	Refinery MDEA filter cartridge	Marathon, Garyville, LA
26	FCC catalyst and fines	R5-FC-02	07-Feb-94	Wet Scrubber Fines	Marathon, Garyville, LA
27	FCC catalyst and fines	R6-FC-01	09-Feb-94	Equil. from unit	Shell, Norco, LA
28	FCC catalyst and fines	R6-FC-02	09-Feb-94	Wet scrubber fines	Shell, Norco, LA
29	Sulfur complex sludge	R6-ME-01	09-Feb-94	Refinery DEA filter cartridge	Shell, Norco, LA
30	Off-spec product & fines from thermal process	R6-TP-01	09-Feb-94	Coke fines.	Shell, Norco, LA
31	Treating clay	R6-CF-01	09-Feb-94	Kerosene	Shell, Norco, LA

Table 2.4. Descriptions of Samples Collected for Record Analysis (continued)

32	Spent caustic	R6-LT-01	09-Feb-94	Naph. Comb. Gas oil & Kero	Shell, Norco, LA
33	Crude oil tank sludge	R6B-CS-01	15-Mar-94	Mix of centrifuge and uncentrifuged	Shell, Norco, LA
34	Unleaded gasoline tank sludge	R6B-US-01	March 31, 94	Water washed solids, collected by refiner	Shell, Norco, LA
35	Catalyst from polymerization	R6B-PC-01	March 15, 94	Dimersol filter	Shell, Norco, LA
36	Catalyst from hydrorefining	R7B-RC-01	March 14, 94	Diesel hydrorefiner	BP, Belle Chase, LA
37	Catalyst from reforming	R7B-CR-01	March 14, 94	Platinum	BP, Belle Chase, LA
38	ASO	R5B-AS-01	March 16, 94	Acid regen settler bottoms, not neutralize	Marathon, Garyville, LA
39	Catalyst from isomerization	R5B-IC-01	March 16, 94	Butamer, platinum	Marathon, Garyville, LA
40	Off-spec sulfur	R7B-SP-01	March 14, 94	From cleaned out tank	BP, Belle Chase, LA
41	Residual oil tank sludge	R8A-RS-01	April 30, 94	CSO and Resid.	Amoco, Texas City
42	Unleaded gasoline tank sludge	R8A-US-01	April 14, 1994	Collected by refinery	Amoco, Texas City
43	Catalyst from hydrocracking	R8A-CC-01	March 30, 94	Hydroproc., 1st stage cracker, CoMo	Amoco, Texas City
44	Catalyst from hydrotreating	R8A-TC-01	March 30, 94	NiMo, landfilled	Amoco, Texas City
45	Off-spec product & fines from thermal processes	R8A-TP-01	March 30, 94	Fines, F&K processed	Amoco, Texas City
46	H2SO4 alkylation sludge	R8B-SS-01	April 30, 94	From Frog pond, not dewatered	Amoco, Texas City
47	HF alkylation sludge	R8B-HS-01	April 30, 94	Not dewatered, dredged	Amoco, Texas City
48	Catalyst from isomerization	R8B-IC-01	April 30, 94	Butamer, Pt	Amoco, Texas City
49	CSO sludge	R9-SO-01,02	May 17, 94	Filters (and blank)	Murphy, Superior, WI
50	Desalting sludge	R9-DS-01	May 17, 94		Murphy, Superior, WI
51	HF alkylation sludge	R9-HS-01	May 17, 94		Murphy, Superior, WI
52	Catalyst from sulfur complex	R7B-SC-01	March 14, 94	SCOT catalyst	BP, Belle Chase, LA
53	Crude oil tank sludge	R10-CS-01	August 26, 94		Ashland, Catletsburg, KY
54	Catalyst from sulfur complex	R11-SC-01	May 10, 94	SCOT, CoMo	ARCO, Ferndale, WA
55	Catalyst from hydrotreating	R11-TC-01	May 10, 94	NiMo, naphtha treater	ARCO, Ferndale, WA
56	Catalyst from reforming	R11-CR-01	May 10, 94	Pt/Rh	ARCO, Ferndale, WA
57	Treating clay	R11-CF-01	May 10, 94	Reformer sulfur trap	ARCO, Ferndale, WA
58	Spent amine	R11-SA-01	May 10, 94	DEA	ARCO, Ferndale, WA
59	Off-spec product & fines from thermal processes	R11-TP-01	May 10, 94	Coke fines	ARCO, Ferndale, WA
60	Treating clay from lube oil	R13-CL-01	April 30, 94	Clay dust	Shell, Deer Park, TX
61	Spent amine	R13-SA-01	April 30, 94	DEA	Shell, Deer Park, TX
62	Spent caustic	R13-LT-01	April 30, 94	Sulfidic	Shell, Deer Park, TX
63	Off-spec product & fines from thermal processes	R12-TP-01	May 12, 94	Coke fines, from trap	Texaco, Anacortes, WA
64	Spent caustic	R12-LT-01	May 12, 94	Cresylic	Texaco, Anacortes, WA
65	Unleaded gasoline tank sludge	R16-US-01	Aug 3, 94		Koch
66	Catalyst from polymerization	R16-PC-01,02	Aug 3, 94	2 catalysts from Dimersol and H2PO4	Koch
67	Crude oil tank sludge	R8C-CS-01	Jul, 94	collected by refinery from tank bottom	Amoco, Texas City
68	Treating clay from extraction	R8D-CI-01	November 15, 94	collected by refinery	Amoco, Texas City
69	Catalyst from hydrotreating	R18-TC-01	October 20, 94	naptha	Ashland, Canton, OH

Table 2.4. Descriptions of Samples ...llected for Record Analysis (continued)

70	Sulfur complex sludge	R18-ME-01	October 14, 94	MEA sludge, collected by refinery	Ashland, Canton, OH
71	Catalyst from isomerization	R18-IC-01	October 20, 94	Penex	Ashland, Canton, OH
72	CSO sludge	R1B-CS-01	August 26, 94	mixed CSO/resid	Marathon, Indianapolis
73	Crude oil tank sludge	R4B-CS-01	August 25, 94	Filter cake sludge	Little America
74	HF alkylation sludge	R15-HS-01	Aug 2, 94	Dredged from pit	Total, Ardmore, OK
75	Catalyst from reforming	R15-CR-01	Aug 2, 94	CCR fines	Total, Ardmore
76	Treating clay from alkylation	R15-CA-01	Aug 2, 94	Butane	Total, Ardmore
77	ASO	R15-AS-01	Aug 2, 94	Neut., skimmed from pit	Total, Ardmore, OK
78	Spent amine	R15-SA-01	Aug 2, 94	MDEA	Total, Ardmore, OK
79	Catalyst from reforming	R14-CR-01	June 7, 94	Cyclic Pt reformer	BP, Toledo, OH
80	Sulfur complex sludge	R14-ME-01	June 7, 94	DEA diatomaceous earth	BP, Toledo, OH
81	Off-spec product & fines from thermal processes	R14-TP-01	June 7, 94	Delayed coking fines	BP, Toledo, OH
82	Spent amine	R14-SA-01	June 7, 94	DEA from sump	BP, Toledo, OH
83	Catalyst from hydrotreating	R3B-TC-01	July 12, 94	Naptha treater	Exxon, Billings, MT
84	Off-spec product & fines from thermal processes	R3B-TP-01	July 12, 94	Fluid coker chunky coke	Exxon, Billings, MT
85	Catalyst from hydrorefining	R21-RC-01	August 31, 94		Chevron, Port Arthur, TX
86	Treating clay from alkylation	R21-CA-01	August 31, 94		Chevron, Port Arthur, TX
87	Catalyst from hydrocracking	R20-CC-01	August 30, 94	H-Oil unit, moving bed	Star, Convent, LA
88	CSO sludge	R20-SO-01	August 30, 94		Star, Convent, LA
89	Crude oil tank sludge	R19-CS-01	September, 94		BP, Belle Chase, LA
90	Desalting sludge	R11B-DS-01	September, 94	to be collected by refinery	ARCO, Ferndale, WA
91	Crude oil tank sludge	R22-CS-01	September 21, 94		Star, Port Arthur, TX
92	Residual oil tank sludge	R22-RS-01	September 21, 94		Star, Port Arthur, TX
93	ASO	R7C-AS-01	October 12, 94		BP, Belle Chase, LA
94	Catalyst from hydrotreating	R22-TC-01	September 21, 94		Star, Port Arthur, TX
95	Spent caustic	R22B-LT-01	October 11, 94	caustic from H2SO4 alky, sulfidic	Star, Port Arthur, TX
96	HF alkylation sludge	R7C-HS-01	October 12, 94	Filter press	BP, Belle Chase, LA
97	Catalyst from isomerization	R23B-CI-01	April 19, 1995	Pt catalyst	Chevron, Salt Lake City
98	Treating clay from isomerization	R23B-IC-01	April 19, 1995	Mole sieve, butamer feed treater	Chevron, Salt Lake City
99	Treating clay from alkylation	R23-CA-01	January 17, 95	propane treater	Chevron, Salt Lake City
100	Off-spec sulfur	R23-SP-01	January 17, 95		Chevron, Salt Lake City
101	Treating clay from clay filtering	R23-CF-01	January 17, 95	diesel washed	Chevron, Salt Lake City
102	Desalting sludge	R24-DS-01	April 20, 1995	Sludge from Lakos separator	Phibro, Houston, TX

Table 2.4. Descriptions of Samples Collected for Record Analysis (continued)

Familiarization Samples					
F1	Spent Caustic	A-SC-01	08-May-93	Comingled.	Marathon, Garyville
F2	Catalyst from hydrotreating	A-HC-01	10-May-93	Cobalt molybdenum.	Marathon, Garyville
F3	Sulfur complex sludge	C-SS-01	23-Jun-93	MEA Reclaimer sludge.	Amoco, Texas City
F4	ASO	C-AS-01	23-Jun-93	Neutralized.	Amoco, Texas City
F5	Crude oil tank sludge	B-TS-01	15-May-93	Filter cake.	Sun, Philadelphia
F6	Sulfuric Acid Catalyst	B-SA-01	15-May-93	Spent from third unit.	Sun, Philadelphia

3.0 PROCESS AND WASTE DESCRIPTIONS

Refineries in the United States vary in size and complexity and are generally geared to a particular crude slate and, to a certain degree, reflect the demand for specific products in the general vicinity of the refinery. Figure 3.1 depicts a hypothetical refinery that employs the major, classic unit operations used in the refinery industry. These unit operations are described briefly below, and in more detail in the remainder of this section. Each subsection is devoted to a major unit operation that generates one or more of the listing residuals of concern and provides information related to the process, a description of the residual and how and why it is generated, management practices used by the industry for each residual, the results of the Agency's characterization of each residual, and summary information regarding source reduction opportunities and achievements.

Storage Facilities: Large storage capacities are needed for feed and products. Sediments can accumulate in these storage units. The consent decree identifies sediments (sludges) from the storage of crude oil, clarified slurry oil, and unleaded gasoline for consideration as listed wastes. Residual oil storage tank sediments were identified as a study residual.

Crude Desalting: Clay, salt, and other suspended solids must be removed from the crude prior to distillation to prevent corrosion and deposits. These materials are removed by water washing and electrostatic separation. Desalting sludge is a study residual.

Distillation: After being desalted, the crude is subjected to atmospheric distillation, separating the crude by boiling point into light ends, naphtha, middle distillate (light and heavy gas oil), and a bottoms fraction. The bottoms fraction is frequently subjected to further distillation under vacuum to increase gas oil yield. No residuals from distillation are under investigation.

Catalytic Cracking: Catalytic cracking converts heavy distillate to compounds with lower boiling points (e.g., naphthas), which are fractionated. Cracking is typically conducted in a fluidized bed reactor with a regenerator to continuously reactivate the catalyst. Cracking catalysts are typically zeolites. The flue gas from the regenerator typically passes through dry or wet fines removal equipment prior to being released to the atmosphere. Catalyst and fines, as well as sediments from storage of clarified slurry oil (the bottoms fraction from catalytic cracking), are listing residuals of concern.

Hydroprocessing: Hydroprocessing includes (1) **hydrotreating and hydrorefining (or hydrodesulfurization)**, which improve the quality of various products (e.g., by removing sulfur, nitrogen, oxygen, metals, and waxes and by converting olefins to saturated compounds); and (2) **hydrocracking**, which cracks heavy materials, creating lower-boiling, more valuable products. Hydrotreating is typically less severe than hydrorefining and is applied to lighter cuts. Hydrocracking is a more severe operation than hydrorefining, using higher temperature and longer contact time, resulting in significant reduction in feed molecular size. Hydroprocessing catalysts are typically some combination of nickel, molybdenum, and cobalt. Typical applications of hydroprocessing include treating distillate to produce low-sulfur diesel fuel, treating naphtha reformer feed to remove catalyst poisons, and treating catalytic cracking unit feed to reduce catalyst deactivation. Hydrotreating and hydrorefining catalysts are listing residuals, while hydrocracking catalyst is a study residual.

Thermal Processes: Thermal cracking uses the application of heat to reduce high-boiling compounds to lower-boiling products. **Delayed (batch)** or **fluid (continuous) coking** is essentially high-severity thermal cracking and is used on very heavy residuum (e.g., vacuum bottoms) to obtain lower-boiling cracked products. (Residuum feeds are not amenable to catalytic processes because of fouling and deactivation.) Products are olefinic and include gas, naphtha, gas oils, and coke. **Visbreaking** is also thermal cracking; its purpose is to decrease the viscosity of heavy fuel oil so that it can be atomized and burned at lower temperatures than would otherwise be necessary. **Other processes** conducting thermal cracking also would be designated as thermal processes. Off-spec product and fines is a listing category from these processes.

Catalytic Reforming: Straight run naphtha is upgraded via reforming to improve octane for use as motor gasoline. Reforming reactions consist of (1) dehydrogenation of cycloparaffins to form aromatics and (2) cyclization and dehydrogenation of straight chain aliphatics to form aromatics. Feeds are hydrotreated to prevent catalyst poisoning. Operations may be semiregenerative, cyclic, or, less frequently, fully-regenerative, continuous, or moving bed catalyst systems. Precious metal catalysts are used in this process. Spent reforming catalyst is a listing residual.

Polymerization: Polymerization units convert olefins (e.g., propylene) into higher octane polymers. Two principal types of polymerization units include fixed-bed reactors, which typically use solid-supported phosphoric acid as the catalyst, and Dimersol® units, which typically use liquid organometallic compounds as the catalyst. Spent polymerization catalyst is a study residual.

Alkylation: Olefins of 3 to 5 carbon atoms (e.g., from catalytic cracking and coking) react with isobutane (e.g., from catalytic cracking) to give high octane products. Sulfuric (H_2SO_4) or hydrofluoric (HF) acid act as catalysts. Spent sulfuric acid, sulfuric acid alkylation sludges, and HF sludges are listing residuals, while spent HF acid, acid soluble oil and treating clays are study residuals.

Isomerization: Isomerization converts straight chain paraffins in gasoline stocks into higher octane isomers. Isomer and normal paraffins are separated; normal paraffins are then catalytically isomerized. Precious metal catalysts are used in this process. Spent catalysts and treating clays are study residuals from this process.

Extraction: Extraction is a separation process using differences in solubility to separate, or extract, a specific group of compounds. A common application of extraction is the separation of benzene from reformate. Treating clay is a study residual from this process.

Lube Oil Processing: Vacuum distillates are treated and refined to produce a variety of lubricants. Wax, aromatics, and asphalts are removed by unit operations such as solvent extraction and hydroprocessing; clay may also be used. Various additives are used to meet product specifications for thermal stability, oxidation resistances, viscosity, pour point, etc. Treating clay is a study residual from this process.

Residual Upgrading: Vacuum tower distillation bottoms and other residuum feeds can be upgraded to higher value products such as higher grade asphalt or feed to catalytic cracking processes. Residual upgrading includes processes where asphalt components are separated from gas oil components by the use of a solvent. It also includes processes where the asphalt value of the residuum is upgraded (e.g., by oxidation) prior to sale. Off-spec product and fines, as well as process sludges, are study residuals from this category.

Blending and Treating: Various petroleum components and additives are blended to different product (e.g., gasoline) specifications. Clay and caustic may be used to remove sulfur, improve color, and improve other product qualities. Spent caustic is a listing residual, while treating clay is a study residual.

Sulfur Recovery: Some types of crude typically contain high levels of sulfur, which must be removed at various points of the refining process. Sulfur compounds are converted to H_2S and are removed by amine scrubbing. The H_2S typically is converted to pure sulfur in a Claus plant. Off-gases from the Claus plant typically are subject to tail gas treating in a SCOT® unit for additional sulfur recovery. Process sludges and spent catalysts are listing residuals; off-spec product and off-spec treating solutions are study residuals.

Light Ends (Vapor) Recovery: Valuable light ends from various processes are recovered and separated. Fractionation can produce light olefins and isobutane for alkylation, n-butane for gasoline, and propane for liquid petroleum gas (LPG). No residuals from this process are under investigation for either the listing determination or the study.

Typical Petroleum Refining Process Flow Diagram

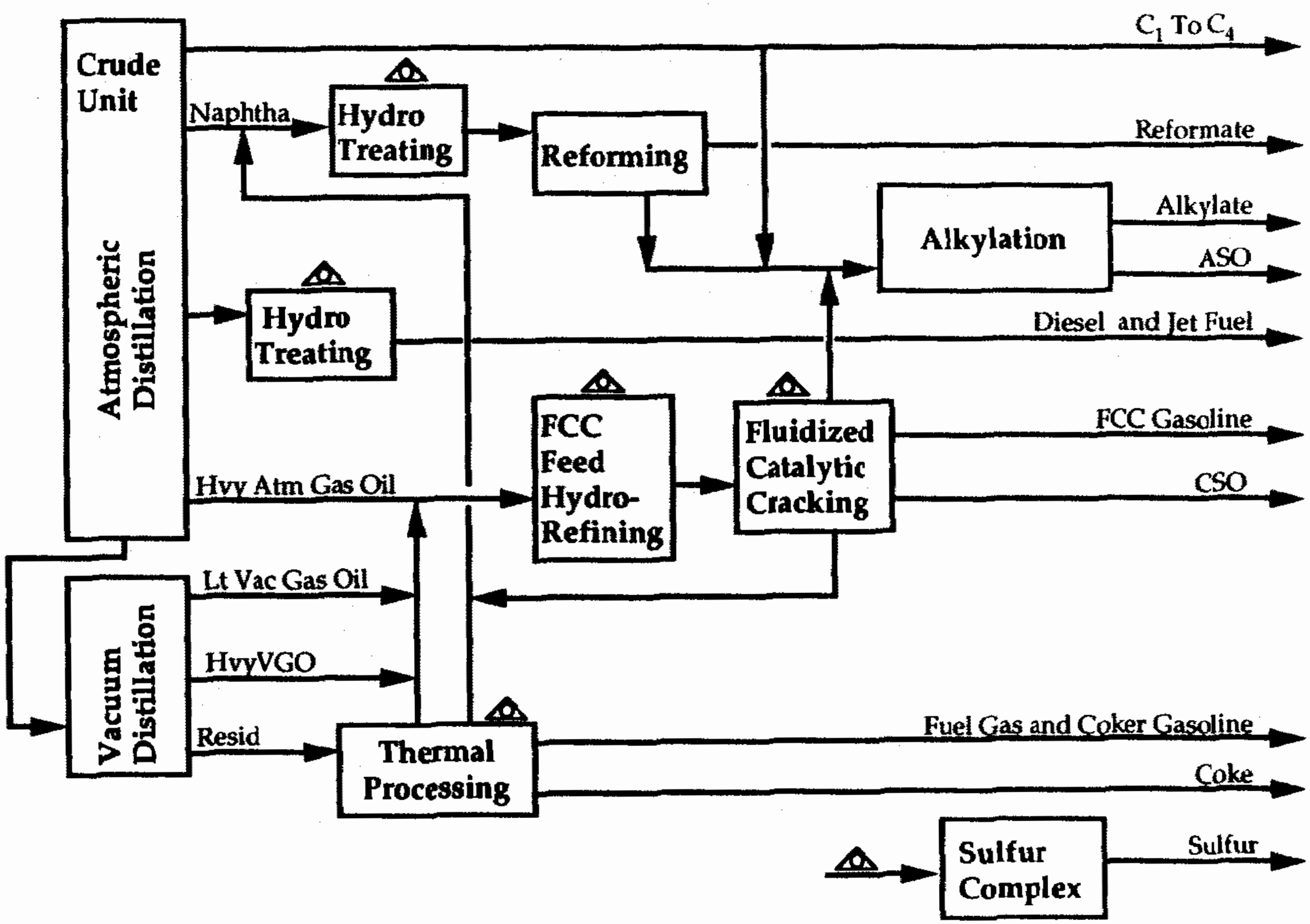


Figure 3.1. Simplified Process Flow Diagram

3.1 TANK STORAGE RESIDUALS

Almost every refinery stores its feed and products in tanks onsite. Occasionally (every 10 to 20 years), tanks require sediment removal due to maintenance, inspection, or sediment buildup. These tank bottoms are removed by techniques ranging from manual shoveling to robotics and filtration.

3.1.1 Crude Oil Storage Tank - Residual 1

In 1992, U.S. refineries reported approximately 1,200 crude oil storage tanks with an average tank volume of about 163,000 barrels. DOE's Petroleum Supply Annual 1992 reported refineries processed just under 5 billion barrels of crude oil or approximately 13.4 million barrels per day.

3.1.1.1 Description

Crude oil tank sediment consists of heavy hydrocarbons, basic sediment and water (BS&W), and entrapped oil that settles to the bottom of the tank. It can be manually removed directly from the tank after drainage of the crude or, commonly, removed using a variety of oil recovery techniques. The recovered oil is returned generally to crude storage while the remaining solids are collected and discarded as waste.

Once a tank is taken out of service, many refineries use *in situ* and *ex situ* oil recovery techniques. Common *in situ* oil recovery techniques include hot distillate washing, and steam stripping. This allows entrapped oil to float to the top of the sediment layer and be recovered prior to removal of the sediment from the tank. *Ex situ* recovery methods are usually performed by a contractor at the tank site and include filtration, centrifuging, and settling. Separated oil is recycled back to the process or sent to the slop oil tanks, and the water phase is sent to the wastewater treatment plant (WWTP). The solids are managed in a variety of ways, including disposal at Subtitle C and D landfills and in land treatment units.

Many refineries reduce tank bottom buildup with in-tank mixers. Mixers keep the sediments or solids continuously in suspension so that they travel with the crude oil to the refining process. The solids are then carried to the desalter where the de-emulsifiers remove them from the crude. This increases the volume of desalting sludge generated.

68% of crude tanks have mixers

In 1992, thirty-three percent of the volume of crude tank bottom sediment was reported to be managed as hazardous. A majority of the residuals were reported as exhibiting the toxicity characteristic for benzene (D018) and/or were ignitable.

3.1.1.2 Generation and Management

The refineries reported generating 22,017 MT of crude oil tank bottom sediment in 1992. Residuals were assigned to be "crude oil tank sediment" if they were assigned a residual identification code of "crude oil tank sediment," corresponding to residual code 01-A in Section VII.2 of the questionnaire. Process wastewaters, decantates, and recovered oils (e.g., from deoiling or dewatering operations) were eliminated from the analysis. These correspond to residual codes 09, 10, and 13 (new) in the questionnaire. Quality assurance was conducted by ensuring that all crude oil tank sediments previously identified in the questionnaire (i.e., in Section V.D) were assigned in Section VII.2. Table 3.1.1 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment modeling. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.1.1 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite land treatment (used for 12.2% of the sediments)
- Offsite land treatment (used for 0.9% of the sediments)
- Offsite Subtitle D landfilling (10.6% of sediments)

An onsite monofill scenario was rejected because of the intermittent (every 10 years) generation frequency which is not typical of waste that tends to be monofilled.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.1.2. The Agency did not model interim storage of crude oil tank sediment because of the infrequency of residual generation and the relatively short time-frame during which the residual is stored onsite prior to final management. EPA observed a number of tank turnarounds during engineering site visits and sampling trips. The refineries generally allotted four to six weeks for a tank turnaround. The first few weeks of the turnaround are used for draining down the tank, *in situ* oil recovery, and preparing the tank for entry. Tank sediments then are removed from the tank (via vacuuming, shovel), sometimes de-oiled (via centrifuge or filter press), and placed in dumpsters. The Agency believes that refineries are motivated to move these dumpsters off of the tank facilities (and to final management) as quickly as possible due to financial constraints (e.g., cost of container rental, contractor costs) and space constraints. As a result, the sediments are probably stored onsite for less than a month prior to final management. Because this time period is so limited, the Agency assumed that the potential for contaminant release and exposure at levels of concern was insignificant in comparison with the long-term risks associated with landfilling and land treatment. Therefore, on-site storage was not modeled in the Agency's risk assessment.

Table 3.1.1. Generation Statistics for Crude Oil Tank Sediment					
Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Discharge to onsite WWTP; discharge to surface water under NPDES	5	0	2,118	529.5	2,115[2]
Disposal offsite in Subtitle D landfill	19	6	2,337.6	123	347
Disposal onsite Subtitle C landfill	1	0	117	117	117
Disposal offsite in Subtitle C landfill	28	2	3,785.6	135.2	400
Discharge to onsite WWT; effluent discharged to evaporation pond	1	0	132	132	132
Offsite incineration[3]	2	0	116	58	82.1
Offsite land treatment	6	1	199	33	100
Onsite land treatment	14	3	2,685.6	192	537.5
Transfer for use as fuel	4	1	578.6	144.6	529
Transfer for use as ingredient in products placed on the land	2	0	43.6	22	32
Transfer with refinery product	1	0	150	150	150
Transfer to other offsite entity	1	0	63.5	63.5	63.5
Recovery onsite[1]	14	15	9,676	666.5	1,000
Other reuse/cover for onsite landfill	1	0	14.6	14.6	14.6
Total Crude Oil Tank Sediment	99	28	22,017	222	400

[1] Other recovery onsite includes recovery in catalytic cracker, coker, or distillation units or in asphalt production.
[2] Sediment removed from tank and trucked to WWTP where it is bled into the treatment system to avoid overloading the biological treatment system.
[3] Hazardous waste incinerators.

Table 3.1.2. Selection of Risk Assessment Modeling Scenario: Crude Oil Tank Sediment

Management	Basis for Consideration in Risk Assessment
Discharge to onsite WWTP; discharge to surface water under NPDES	Not modeled. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be captured by existing hazardous waste listings and further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Disposal offsite in Subtitle D landfill	Modeled
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Discharge to onsite WWT; effluent discharged to evaporation pond	Not modeled, waste is discharged to wastewater treatment (see above). Minimal volume, reported only by one facility.
Recovery onsite[1]	Proposed excluded management practice
Offsite land treatment	Modeled
Onsite land treatment	Modeled
Transfer for use as fuel	Not modeled. Already regulated if characteristic. Minimal volume reported.
Transfer for use as ingredient in products placed on the land	Not modeled. Already regulated if characteristic. Minimal volume and already modeled land application in land treatment scenario.
Transfer with refinery product	Not modeled. Proposed excluded management practice.
Offsite incineration	Not modeled, hazardous waste incineration - no incremental risk to control
Recovery onsite via distillation	Not modeled, exempt management practice
Transfer to other offsite entity	Not modeled, exempt management practice. Minimal volume.
Other reuse/cover for onsite landfill	Not modeled. Minimal volume, unlikely to present risk. Land application and landfill scenarios modeled.

[1] Other recovery onsite includes recovery in catalytic cracker, coker, or distillation units.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.1.3 provides a summary of the data for the targeted management practices used in the risk assessments for the crude oil tank sediments. Appendix C summarizes §3007 data regarding runon/runoff controls for these units.

Many refineries conduct de-oiling of crude oil tank sediment, both before and after removal from the storage tank. The Agency evaluated whether de-oiling has any impact on the risks associated with the disposed sediment. The Agency hypothesized that de-oiling might reduce toxicant concentrations for certain toxicant fractions (e.g., volatiles), although others could be concentrated (e.g., metals). Samples were collected of sediments with and without de-oiling after removal from the storage tanks (described further in Section 3.1.1.3). Total oil and grease content was analyzed for each sample (see also Section 3.1.1.3).

The following conclusions were reached regarding the effects of de-oiling on the risks associated with this residual:

(1) De-oiling reduces volume, which, if all other factors were held constant, would tend to reduce the risk modeled. The average de-oiled crude oil tank sediment volume is 120 MT, while the average oily sediment volume is 350 MT.

(2) De-oiled sediments are predominantly sent for onsite land treatment (37%), disposed offsite in a Subtitle D landfill (24%), or disposed offsite in Subtitle C landfill (17%). Oily sediments are more liked to be recycled to the process (57%), disposed of in an offsite Subtitle C landfill (17%), and discharged to onsite WWTP (14%).

(3) The oil and grease levels remaining in the sediment after de-oiling are highly variable among refineries (4.87 to 41.1 percent), even when similar techniques are used. One de-oiled record sample had oil and grease concentrations at the same level as another oily record sample.

(4) The Agency observed a wide range of effectiveness and combinations of *in situ* and *ex situ* techniques. At certain refineries (perhaps many), centrifuging and other types of mechanical de-oiling techniques are only used on those sediments which fail the "paint filter test" which is used as a surrogate for recoverable oil. As a result, the upper layers of tank sediment are subjected to *ex situ* de-oiling, while the lower layers are not de-oiled. Tank operating conditions may also affect sediment content, such as the use of in-tank mixers and ambient temperature at the time of sediment removal.

After considering all of these factors, the Agency determined that differentiating between oily and de-oiled sediments was inappropriate.

Table 3.1.3. Management Practices Targeted for Risk Assessment

Parameters	# of Fac.	# of RC	# RC w/ Unreported Volume	Total Volume (MT)	10th % Volume (MT)	50th % Volume (MT)	90th % Volume (MT)
Offsite Subtitle D Landfill[3]	12	19	6	2,337.6	—	29.75	632
Offsite Land Treatment Unit[3]	4	6	1	199	—	44	100
Onsite Land Treatment Unit[1,3]	9	14	3	2,685.6	—	38	1,839
	Characteristics						
	Surface Area (acres)				3.5	14.5	32
	Depth of Incorporation (in)				6	9.5	13.5
	Amount Applied (1992 MT)[2]				0.3	272	12,000
	Methods of Incorporation: Disking (16) Subsurface Injection (1) Springtooth Harrow (1)						
	# of Landfills: 18						
	Aquifer Information						
	Depth to Aquifer (ft)				12.5	17.5	150
	Distance to Private Well (ft)				2,000	9,000	26,400
	Population Using Private Well				0	1.5	300
	Distance to Public Well (ft)				2,000	18,480	52,800
	Population Using Publio Well				250	250	250
	# of Aquifers: 14						
	Source: / Public / Private Unreported 9 7 Uppermost 1 3 Lowermost 4 4 Combination — —						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (4) Not considered a potential source of drinking water (9) Unreported (1)						

[1] The number of onsite land treatment units characterized in Table 3.1.3 is greater than indicated in Table 3.1.1 which focuses only on volumes generated in 1992. Table 3.1.3 incorporates data from all onsite land treatment units receiving crude oil tank sediment in any year reported in the §3007 survey.

[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the crude tank sediment and not just the tank sediment alone.

[3] The mean and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream from one refinery may be disposed of in one management unit causing the 90th percentile number actually to be the sum of 2 or 3 waste volumes).

Table 3.1.4. Crude Oil Tank Sediment Physical Properties					
Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	116	182	6	7.4	8.6
Reactive CN, ppm	66	232	0.1	34.5	120
Reactive S, ppm	82	216	0.1	232.4	500
Flash Point, °C	101	196	29.4	70	100
Oil and Grease, vol%	106	192	5	34.3	80
Total Organic Carbon, vol%	39	259	0	23	65
Viscosity, lb/ft-sec	5	289	0.02	12.5	60
Specific Gravity	76	222	0.84	1.52	1.86
BTU Content, BTU/lb	54	244	100	7,281	14,499
Aqueous Liquid, %	154	144	0	19.2	50
Organic Liquid, %	157	141	0	31.8	80
Solid, %	190	108	9.5	54.5	100
Particle >60 mm, %	21	277	0	19.2	100
Particle 1-60 mm, %	24	274	0	18.5	50
Particle 100 μm-1 mm, %	24	274	0	52.25	98
Particle 10-100 μm, %	24	274	0	17.2	45
Particle <10 μm, %	17	281	0	1	7
Mean Particle Diameter, microns	13	284	10	1,683	1000

3.1.1.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.1.4 summarizes the physical properties of the crude oil tank sediment as reported in Section VII.A of the §3007 survey.
- Six record samples of actual sediments were collected and analyzed by EPA. These sediments represent the various types of oil recovery typically used by the industry and are summarized in Table 3.1.5.

Table 3.1.6 provides a summary of the characterization data collected under this sampling effort. All the record samples collected are believed to be representative of the crude oil tank sediment as generated. The samples collected of the composite of oily and de-oiled sediment are representative of industry de-oiling practices. It is common practice for the refinery to recover oil from the top layers of sediment where there is a high percentage of free oil, but as the top layers are removed the bottom layers will contain less free oil and more asphaltenes. At most refineries, the paint filter test is performed on the sediment throughout the tank cleaning/sediment de-oiling process. Once the sediment passes the paint filter test, the sediment de-oiling (centrifuging/filtering) process is stopped and the remainder of the sediment is removed directly from the tank without de-oiling. Therefore, refineries may perform oil recovery only at the beginning of tank cleaning operations.

As illustrated in Table 3.1.6, two samples exhibited the characteristic for benzene. Oil and grease content ranged between 4 and 41 percent. Only constituents detected in at least one sample are shown in this table.

Table 3.1.5. Crude Oil Tank Sediment Record Sampling Locations

Sample No.	Facility	Description: Oil Recovery	Oil & Grease Content
R6B-CS-01	Shell, Norco, LA	Composite of non-centrifuged and centrifuged sediment.	24.2%
R10-CS-01	Ashland, Catlettsburg, KY	Liquidized and recycled to the catalytic cracker. Sample collected prior to liquification.	41.1%
R8C-CS-01	AMOCO, Texas City, TX	Collected directly from the tank by refinery personnel.	24.7%
R4B-CS-01	Little America, Casper, WY	Composite of centrifuged and non-centrifuged sediment.	15.4%
R19-CS-01	Pennzoil, Shreveport, LA	Filtered.	14.4%
R22-CS-01	Star Enterprises, Port Arthur, TX	De-oiled using a shaker.	4.87%

Table 3.1.6. Crude Oil Tank Sediment Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.		R6B–CS–01		R6C–CS–01		R4B–CS–01		R10–CS–01		R19–CS–01		R22–CS–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acrolein	107028	<	31,250	<	12,500	<	2,500		24,000	<	600	<	2,500	8,420	24,000	9,882	15,195	1
Benzene	71432		69,000		220,000		8,200		52,000	J	660	<	2,500	58,727	220,000	83,960	109,319	
n-Butylbenzene	104518		32,000		50,000		37,000		49,000	J	1,000		6,900	29,317	50,000	20,908	41,918	
sec-Butylbenzene	135988		21,000		36,000		13,000		25,000	J	270	J	3,900	16,528	36,000	13,470	24,645	
Ethylbenzene	100414		79,000		260,000		38,000		120,000	J	430		25,000	67,072	260,000	94,680	144,123	
Isopropylbenzene	98828		32,000		70,000		15,000		41,000	J	420		4,100	27,420	70,000	25,908	43,032	
p-Isopropyltoluene	99876		19,000		31,000		12,000		30,000	J	250		5,800	16,342	31,000	12,629	23,951	
Methyl ethyl ketone	78933		6,250	<	12,500	<	2,500		29,000	<	600	<	2,500	8,892	29,000	10,722	15,352	
n-Propylbenzene	103651		40,000		110,000	<	2,500	<	1,250	<	600		11,000	27,558	110,000	43,064	53,507	
Toluene	108883		200,000		400,000		31,000		140,000	J	340	<	2,500	128,973	400,000	155,411	222,620	
1,2,4-Trimethylbenzene	95636		150,000		330,000		49,000		160,000		4,100		64,000	126,517	330,000	116,392	196,651	
1,3,5-Trimethylbenzene	108678		120,000		160,000		73,000		100,000		1,700		7,100	76,967	160,000	62,991	114,923	
o-Xylene	95476		150,000		320,000		67,000		170,000	J	630	<	2,500	118,405	320,000	121,801	191,799	
m,p-Xylenes	108383 / 106423		320,000		830,000		180,000		390,000		1,400		18,000	289,900	830,000	307,205	475,014	
Naphthalene	91203		84,000		210,000		65,000		58,000		2,400		5,100	70,750	210,000	75,620	116,437	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R6B–CS–01		R6C–CS–01		R4B–CS–01		R10–CS–01		R19–CS–01		R22–CS–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	<	50		270		210		120		140	<	50	140	270	88	193	
Benzene	71432		1,700		1,600		130		580	J	32	<	50	679	1,700	777	1,147	
Ethylbenzene	100414		240		370	J	90		180	<	50		210	190	370	114	259	
Toluene	108883		1,900		1,600		230		930	<	50	<	50	793	1,900	814	1,284	
1,2,4-Trimethylbenzene	95636		260		160		190		150	J	24		100	147	260	80	196	
1,3,5-Trimethylbenzene	108678		100	J	54	<	50	J	45	<	50	<	50	58	100	21	71	
Methylene chloride	75092	<	50	<	50	<	50	<	50		170	<	50	70	170	49	100	
o-Xylene	95476		580		480		170		310	<	50	<	50	273	580	223	408	
m,p-Xylene	108383 / 106423		1,500		1,300		450		670	<	50		120	682	1,500	603	1,045	
Naphthalene	91203		150	J	97		300	J	61	J	38	<	50	116	300	99	175	

Semivolatile Organics – Method 8270B µg/kg

	CAS No		R6B–CS–01		R6C–CS–01		R4B–CS–01		R10–CS–01		R19–CS–01		R22–CS–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	<	10,313		13,000		99,000	<	49,500	<	11,500	<	413	30,621	99,000	37,505	53,221	
Anthracene	120127	<	10,313	<	4,125		90,000	<	49,500	<	11,500	<	413	27,642	90,000	35,275	48,898	
Benz(a)anthracene	56553	<	10,313	<	4,125		31,000	<	49,500	<	11,500	<	413	11,470	31,000	11,821	19,574	1
Benzofluoranthene (total)	NA	<	10,313	J	5,900		29,000	<	49,500	<	11,500	<	413	11,425	29,000	10,746	18,792	1
Benzo(g,h,i)perylene	191242	<	10,313		18,000		14,000	<	49,500	<	11,500	<	413	10,845	18,000	6,533	15,324	1
Benzo(a)pyrene	50328	J	17,000	J	6,600		26,000	<	49,500	<	11,500	<	413	12,303	26,000	9,801	19,022	1
Carbazole	86748	<	20,625	<	8,250		140,000	<	99,000	<	23,500	<	825	48,700	140,000	56,951	83,017	
Chrysene	218019	J	13,000		28,000		42,000	<	49,500	<	11,500	<	413	19,163	42,000	16,329	30,377	1
Dibenzofuran	132649	<	10,313		12,000	<	4,125	J	11,000	<	11,500	<	413	8,225	12,000	4,793	11,113	
Dibenz(a,h)anthracene	53703	<	10,313	<	4,125	J	3,700	<	49,500	<	11,500	<	413	2,056	3,700	2,325	7,116	1, 2
3,3'-Dichlorobenzidine	91941	<	11,875	<	4,750	<	4,750	<	57,000	<	13,500		1,800	1,800	1,800	NA	NA	1
Fluoranthene	206440	<	10,313	J	6,400		72,000	<	49,500	<	11,500	<	413	25,021	72,000	28,637	42,397	
Fluorene	86737		37,000		32,000		62,000	J	29,000	<	11,500		1,300	28,800	62,000	21,144	41,541	
Indeno(1,2,3-cd)pyrene	193395	<	10,313	J	3,000		15,000	<	49,500	<	11,500	<	413	8,045	15,000	6,107	12,231	1
Phenanthrene	85018		73,000		76,000		380,000	J	47,000	<	11,500		7,300	99,133	380,000	140,666	183,895	
Pyrene	129000	J	12,000		120,000		72,000	<	49,500	<	11,500	<	413	44,235	120,000	45,978	71,941	
1-Methylnaphthalene	90120		240,000		210,000		1,300,000		340,000	<	23,500		19,000	355,417	1,300,000	479,640	644,437	
2-Methylnaphthalene	91576		300,000		450,000		2,100,000		370,000	J	5,700		7,600	538,883	2,100,000	787,035	1,013,130	
2-Methylchrysene	3351324	J	8,300		21,000	J	7,300	<	99,000	<	23,500	<	825	9,356	21,000	8,440	16,269	1
3/4-Methylphenol	NA	<	10,313	<	4,125		12,000	<	49,500	<	11,500	<	413	7,670	12,000	5,139	11,193	1
Naphthalene	91203		180,000		150,000		280,000		150,000	<	11,500		6,100	129,600	280,000	105,064	192,909	

CRUDE TANK SLUDGE

TCLP Semivolatile Organics -- Methods 1311 and 8270B µg/L

	CAS No.	R6B-CS-01	R6C-CS-01	R4B-CS-01	R10-CS-01	R19-CS-01	R22-CS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	< 50	< 50	J 19	< 50	< 50	< 50	19	19	NA	NA	1
Di-n-butylphthalate	84742	< 50	< 50	< 50	< 50	J 52	J 15	45	52	14	53	2
Carbazole	86748	< 100	< 100	J 73	< 100	< 100	< 100	73	73	NA	NA	1
2,4-Dimethylphenol	105679	< 50	< 50	J 39	< 50	< 50	< 50	39	39	NA	NA	1
Dimethyl phthalate	131113	< 50	< 50	< 50	J 12	< 50	< 50	12	12	NA	NA	1
Fluorene	86737	< 50	< 50	J 18	< 50	< 50	< 50	18	18	NA	NA	1
1-Methylnaphthalene	90120	J 33	J 27	640	J 39	< 100	J 13	142	640	240	290	
2-Methylnaphthalene	91576	J 38	J 50	890	J 39	< 50	J 12	180	890	348	390	
2-Methylphenol	95487	< 50	< 50	J 31	< 50	< 50	< 50	31	31	NA	NA	1
3/4-Methylphenol	NA	< 50	< 50	490	< 50	< 50	< 50	123	490	180	232	
Naphthalene	91203	J 65	J 77	500	J 59	< 50	J 14	128	500	184	238	
Phenanthrene	85018	< 50	< 50	J 27	< 50	< 50	< 50	27	27	NA	NA	1
Phenol	108952	< 50	< 50	160	J 47	< 50	< 50	68	160	45	95	

Total Metals -- Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R6B-CS-01	R6C-CS-01	R4B-CS-01	R10-CS-01	R19-CS-01	R22-CS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	2,200.0	8,600.0	1,600.0	330.0	1,600.0	780.0	2,551.7	8,600.0	3,041.4	4,384.4	
Antimony	7440360	< 6.0	< 6.0	< 12.0	< 6.0	< 6.0	15.0	8.5	15.0	4.0	10.9	
Arsenic	7440382	6.0	8.3	32.0	5.7	18.0	19.0	14.8	32.0	10.3	21.0	
Barium	7440393	4,400.0	300.0	950.0	820.0	1,200.0	330.0	1,333.3	4,400.0	1,543.2	2,283.2	
Cadmium	7440439	1.6	1.2	< 1.0	< 0.5	< 0.5	2.0	1.1	2.0	0.6	1.5	
Calcium	7440702	10,000.0	14,000.0	11,000.0	2,300.0	9,900.0	25,000.0	12,033.3	25,000.0	7,436.3	16,514.3	
Chromium	7440473	49.0	310.0	51.0	9.7	150.0	100.0	111.6	310.0	108.6	177.0	
Cobalt	7440484	16.0	360.0	< 10.0	< 5.0	17.0	27.0	72.3	360.0	141.1	157.4	
Copper	7440508	130.0	170.0	190.0	73.0	320.0	870.0	292.2	870.0	294.7	469.8	
Iron	7439896	18,000.0	25,000.0	200,000.0	26,000.0	120,000.0	300,000.0	114,833.3	300,000.0	115,676.1	184,536.8	
Lead	7439921	220.0	44.0	320.0	44.0	870.0	60.0	259.7	870.0	319.6	452.2	
Magnesium	7439954	1,200.0	1,400.0	< 1,000.0	< 500.0	< 500.0	4,200.0	1,466.7	4,200.0	1,388.0	2,303.1	
Manganese	7439965	140.0	160.0	760.0	130.0	590.0	2,200.0	661.7	2,200.0	799.7	1,143.6	
Mercury	7439976	0.5	2.5	0.7	0.3	1.8	2.5	1.4	2.5	1.0	2.0	
Molybdenum	7439987	< 6.5	860.0	< 13.0	< 6.5	23.0	22.0	156.5	860.0	353.5	371.5	
Nickel	7440020	64.0	380.0	61.0	15.0	82.0	74.0	112.7	380.0	133.0	192.8	
Sodium	7440235	2,800.0	6,300.0	< 1,000.0	< 500.0	1,100.0	1,000.0	2,116.7	6,300.0	2,195.6	3,439.8	
Vanadium	7440622	10.0	1,400.0	< 10.0	12.0	13.0	< 5.0	241.7	1,400.0	567.5	583.6	
Zinc	7440666	670.0	640.0	1,000.0	360.0	670.0	1,200.0	756.7	1,200.0	297.2	935.8	

TCLP Metals -- Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6B-CS-01	R6C-CS-01	R4B-CS-01	R10-CS-01	R19-CS-01	R22-CS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Barium	7440393	< 1.00	2.40	< 1.00	< 1.00	2.70	< 1.00	1.52	2.70	0.81	2.00	
Calcium	7440702	< 25.00	550.00	260.00	< 25.00	120.00	270.00	208.33	550.00	199.11	328.31	
Iron	7439896	1.40	110.00	77.00	6.40	55.00	800.00	174.97	800.00	309.00	361.16	
Manganese	7439965	0.15	1.30	2.50	0.59	0.69	7.80	2.17	7.80	2.88	3.90	
Zinc	7440666	0.26	0.21	0.37	< 0.10	0.83	< 0.10	0.31	0.83	0.27	0.48	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.1.1.4 Source Reduction

In situ oil recovery techniques can greatly reduce the total amount of crude oil tank sediment to be disposed as well as reduce volatile constituents such as benzene. As discussed above, recovery methods include distillate washing, nonpetroleum solvent washing, water wash with surfactant, and steam stripping. These operations allow entrapped oil to float to the top of the sediment layer and be recovered prior to removal from the tank. Separated oil is recycled back to the process or sent to the slop oil tanks, and the water phase is sent to the WWTP.

As reported in the §3007 survey, the average amount of oily sediment (not centrifuged/filtered/settled) generated is 350 MT while the average quantity for sediment that was centrifuged, filtered, or settled was 120 MT, a 66% volume reduction.

Another method to reduce tank bottom buildup in tanks is to install mixers. Mixers keep the sediments or solids continuously in suspension so that they travel with the crude oil to the refining process. The solids are then carried to the desalter where they result in an increase the volume of desalting sediment generated.

3.1.2 Unleaded Gasoline Storage - Residual 2

In 1992, 146 U.S. refineries reported approximately 1,400 unleaded gasoline storage tanks with an average capacity of 237,000 barrels, according to the §3007 survey. The survey requested that the refineries report only finished product tanks and not tanks that store intermediate products such as alkylate. Facilities that did not report unleaded gasoline storage include lube plants, asphalt plants, and facilities that do not perform finished gasoline blending onsite.

3.1.2.1 Description

Approximately every 10 years, gasoline storage tanks are taken out of service to inspect the tank's integrity. At that time, the product is drained from the tank and the tank is cleaned.

Unleaded gasoline tank sediment consists of tank scale and rust. A typical cleaning procedure is to wash the inside of the tank with water (to decrease occupational benzene levels), discharging the water to the sewer, and sweep or scrape the remaining solids for disposal. It is not uncommon for no solids to be generated.

As with crude oil storage tanks, mixers are also installed in unleaded gasoline tanks to reduce tank bottoms sediment accumulation. However, due to the nature of the gasoline production process, very few solids should be in the gasoline.

Once the tank sediment has been removed and any repairs have been made, some refineries paint the tank's interior with an epoxy to protect the tank and reduce rust and scale generation.

In 1992, 25 percent of the volume of unleaded gasoline sediment was reported to be hazardous. A majority of these residuals were reported as exhibiting the toxicity characteristic for benzene (D018) and/or the ignitability characteristic.

3.1.2.2 Generation and Management

The refineries reported generating 3,583 MT of unleaded gasoline tank bottom sediment in 1992. Residuals were assigned to be "unleaded gasoline tank sediment" if they were assigned a residual identification code of "unleaded gasoline tank sediment," corresponding to residual code 01-C in Section VII.2 of the questionnaire. Process wastewaters and decantates (e.g., from deoiling or dewatering operations) were eliminated from the analysis. These correspond to residual codes 09 and 10 in the questionnaire. Quality assurance was conducted by ensuring that all unleaded gasoline tank sediments previously identified in the questionnaire (i.e., in Section V.D) were assigned in Section VII.2. Table 3.1.7 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.1.7. Generation Statistics for Unleaded Gasoline Tank Sediment					
Final Management	**# of Streams**	**# of Unreported Volume Streams**	**Total Volume (MT)**	**Average Volume (MT)**	**90th Percentile Volume (MT)**
Discharge to onsite WWTP; ultimate discharge to surface water	16	9	2,091	130.7	120
Disposal offsite in Subtitle D landfill	28	7	625	22.3	47.7
Disposal onsite Subtitle D landfill	3	0	8.4	2.8	6.6
Disposal onsite and offsite in Subtitle C landfill	27	3	106	5.9	19
Offsite incineration[1]	8	0	176.7	22	60.7
Other disposal onsite	1	0	18	18	18
Recovery onsite	4	9	92.7	23	30
Offsite land treatment	8	0	98.22	12.3	66
Onsite land treatment	15	2	118	8	20.6
Transfer for use as fuel	1	0	195	195	195
Total unleaded gasoline sediment	111	30	3,583	32.3	66

[1] Four facilities send wastes to 3 hazardous waste incinerators.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.1.8 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite land treatment (used for 3.1% of sediment)
- Offsite Subtitle D landfilling (16.5% of sediment)
- Onsite Subtitle D landfilling (0.2% of sediment)

An onsite monofill scenario was rejected because the intermittent (every 10 years) generation frequency and small quantities are not typical of wastes that tend to be monofilled.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.1.8.

Table 3.1.8. Selection of Risk Assessment Modeling Scenario: Unleaded Gasoline Tank Sediment

Waste	Basis for Consideration in Risk Assessment
Discharge to onsite WWTP; ultimate discharge to surface water	Not modeled. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be captured by existing hazardous waste listings and further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Disposal offsite in Subtitle D landfill	Modeled
Disposal onsite in Subtitle D landfill	Modeled
Disposal onsite and offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite incineration	Not modeled, hazardous waste incinerators - no incremental risk to control
Other disposal onsite	Not modeled, minimal volume
Recovery onsite	Proposed excluded management practice
Offsite land treatment	Modeled
Onsite land treatment	Modeled
Transfer for use as fuel	Not modeled, already regulated if characteristic, minimal volume reported.

The Agency evaluated whether it was necessary to model short-term on-site storage of unleaded gasoline tank sediment prior to final management. Using the same logic described in the previous discussion of the selection of management practices to be modeled for crude oil tank sediment, EPA determined that the potential for contaminant release and exposure at levels of concern was insignificant in comparison with the long-term risks associated with landfilling and land treatment. Therefore, on-site storage was not modeled in the Agency's risk assessment.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.1.9 provides a summary of the data for the targeted management practices used in the risk assessment.

Table 3.1.9. Management Practices Targeted for Risk Assessment							
Unleaded Gasoline Tank Sediment							
Parameters	# of Fac.	# of RC	# RC w/ Unreported Volume	Total Volume (MT)	10th % Volume (MT)	50th % Volume (MT)	90th % Volume (MT)
Offsite Land Treatment[3]	3	8	0	98.22	—	2.22	94
Onsite Land Treatment Unit[1,3]	9	15	2	118	—	2	57
	Characteristics						
	Surface Area (acres)				2	14.5	32.3
	Depth of Incorporation (in)				4	9	12
	Amount Applied (1992 MT)[2]				2	345	12,000
	Methods of Incorporation: Disking (13) Subsurface Injection (1) Springtooth Harrow (1)						
	# of Land Treatment Units: 15						
	Aquifer Information						
	Depth to Aquifer (ft)				6	15.5	97
	Distance to Private Well (ft)				3,000	4,390	10,000
	Population Using Private Well				1	150.5	300
	Distance to Public Well (ft)				7,920	34,325	52,800
	Population Using Public Well				—	—	—
	# of Aquifers: 13						
	Source: Public Private Unreported 9 11 Uppermost 1 — Lowermost 2 1 Combination 1 1						
	Classification of Uppermost Aquifer: Current of potential source of drinking water (3) Not considered a potential source of drinking water (9) Unreported (1)						

Table 3.1.9. Management Practices Targeted for Risk Assessment							
Unleaded Gasoline Tank Sediment							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfill[1,3,4]	18	31	7	633.4	—	6.25	72.7
	Onsite Landfill Characteristics						
	Surface Area (acres)				3.7	7.5	36
	Remaining Capacity (cu.yd.)				25,088	80,000	6,500,000
	Percent Remaining Capacity				0.7	12	25
	Total Capacity (cu.yd.)				85,000	168,950	8,000,000
	Number of Strata in Completed Unit				0	5.25	400
	Depth Below Grade (ft)				0	6	15
	Height Above Grade (ft)				3	13	72
	# of Landfills: 6						
	Aquifer Information						
	Depth to Aquifer (ft)				8.5	12	166
	Distance to Private Well (ft)				2,500	2,500	2,500
	Population Using Private Well				2	2	2
	Distance to Public Well (ft)				15,840	15,840	15,840
	Population Using Public Well				—	—	—
	# of Aquifers: 6						
	Source: Public / Private Unreported 3 / 5 Combination 3 / 1						
	Classification of Uppermost Aquifer: Current of potential source of drinking water (1) Not considered a potential source of drinking water (5)						

[1] The number of onsite land treatment units and landfills characterized in Table 3.1.9 is greater than indicated in Table 3.1.7 which focuses only on volumes generated in 1992. Table 3.1.9 incorporates data, respectively, from all onsite land treatment units, and all onsite landfills, receiving unleaded tank sediment in any year reported in the §3007 survey.
[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the unleaded tank sediment and not just the tank sediment alone.
[3] The mean and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream from one refinery may be disposed of in one management unit causing the 90th percentile number actually to be the sum of 2 or 3 waste volumes).
[4] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.1.2.3 Characterization

Due to the small amount of sediment typically generated during turnaround and, at times, the absence of sediment, samples of unleaded gasoline sediments were very difficult to obtain. The number of refineries chosen for record sampling was expanded to increase the availability of these hard-to-find residuals; however, the newly targeted facilities did not increase the procurability of unleaded tank sediment.

Two sources of residual characterization were developed during the industry study:

- Table 3.1.10 summarizes the physical properties of the tank sediment as reported in Section VII.A of the §3007 survey.
- Three samples of unleaded gasoline tank sediment were collected. These samples were collected after the tanks had been water-washed. Table 3.1.11 provides the location and description of the samples collected.

Table 3.1.10. Unleaded Gasoline Tank Sediment Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	109	172	5.2	7.5	10
Reactive CN, ppm	57	224	0	30.25	50
Reactive S, ppm	65	216	0	41.7	125
Flash Point, °C	77	204	20	57.7	93
Oil and Grease, vol%	77	204	0.5	10.81	20
Total Organic Carbon, vol%	44	237	0	11.1	20
Specific Gravity	68	213	1.0	1.4	2.27
BTU Content, BTU/lb	27	254	100	4,088	16,155
Aqueous Liquid, %	156	125	0	23.9	70
Organic Liquid, %	150	131	0	7.31	20
Solid, %	190	91	20	72.8	100
Particle >60 mm, %	22	259	0	25.2	89
Particle 1-60 mm, %	24	257	0	46.4	100
Particle 100 µm-1 mm, %	23	258	0	35.3	100
Particle 10-100 µm, %	19	262	0	13.7	50
Particle <10 µm, %	19	262	0	7.9	50
Mean Particle diameter, microns	12	269	0	1,294	500

Table 3.1.11. Unleaded Gasoline Sediment Record Sampling Locations		
Sample Number	**Location**	**Description**
R6B-US-01	Shell, Norco, LA	Water-washed solids: collected by refinery
R8A-US-01	Amoco, Texas City, TX	Water-washed solids: collected by refinery
R16-US-01	Koch, St. Paul, MN	Drummed, dry, light-brown, water-washed solids

The 3 samples collected are believed to be representative of the industry. Table 3.1.12 provides the characterization data for this sampling effort. Only constituents detected in at least one sample are shown in this table. Of the 3 unleaded gasoline sediment samples collected, one sample exhibited the toxicity characteristic for benzene. Unleaded gasoline tank sediment has a low organic content because the tank is water-washed prior to tank entry. High iron concentrations can be attributed to the rust and scale of the tank.

3.1.2.4 Source Reduction

As with crude oil tank sediments, mixers have reduced the volume of sediment generated. The mixers are used to suspend the solids in the product, reducing the amount of solids that may settle to the bottom of the tank.

50% of unleaded gasoline storage tanks have mixers

Table 3.1.12. Unleaded Gasoline Storage Tank Sediment Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432	43,000	110,000	J 2,700	51,900	110,000	54,201	110,918	2
n–Butylbenzene	104518	73,000	210,000	77,000	120,000	210,000	77,968	204,898	
sec–Butylbenzene	135988	J 12,000	< 25,000	J 7,600	14,933	25,000	8,967	24,698	
Ethylbenzene	100414	290,000	450,000	58,000	266,000	450,000	197,099	480,818	2
Isopropylbenzene	98828	27,000	< 25,000	J 11,000	21,000	27,000	8,718	30,493	2
n–Propylbenzene	103651	130,000	230,000	38,000	132,667	230,000	96,028	237,230	2
Toluene	108883	690,000	740,000	85,000	505,000	740,000	364,569	901,994	2
1,2,4–Trimethybenzene	95636	740,000	1,300,000	400,000	813,333	1,300,000	454,459	1,308,186	2
1,3,5–Trimethybenzene	108678	230,000	460,000	160,000	283,333	460,000	156,950	454,234	
o–Xylene	95476	440,000	640,000	240,000	440,000	640,000	200,000	657,777	2
m,p–Xylenes	108383 / 106423	1,400,000	1,300,000	610,000	1,103,333	1,400,000	430,155	1,571,722	2
Naphthalene	91203	170,000	350,000	190,000	236,667	350,000	98,658	344,093	2

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Methylene chloride	75092	< 50	150	< 50	83	150	58	148	
Benzene	71432	600	1,600	J 55	752	1,600	784	1,605	2
Ethylbenzene	100414	1,100	1,500	290	963	1,500	616	1,635	2
n–Propylbenzene	103651	240	270	J 60	190	270	114	314	2
Toluene	108883	1,700	8,000	950	3,550	8,000	3,872	7,766	
1,2,4–Trimethybenzene	95636	1,500	2,300	1,200	1,667	2,300	569	2,286	
1,3,5–Trimethybenzene	108678	560	700	300	520	700	203	741	2
o–Xylene	95476	1,900	3,000	1,400	2,100	3,000	819	2,991	
m,p–Xylene	108383 / 106423	3,200	6,100	2,700	4,000	6,100	1,836	5,999	
Naphthalene	91203	920	1,000	640	853	1,000	189	1,059	2

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	J 760	J 900	J 250	643	900	346	1,020	2
Anthracene	120127	J 760	< 1,650	< 165	463	760	421	1,378	1, 2
Bis(2–ethylhexyl)phthalate	117817	7,600	< 1,650	< 165	3,136	7,600	3,935	7,423	
Indene	95136	42,000	72,000	J 890	38,297	72,000	35,699	77,189	2
Fluorene	86737	J 1,400	J 1,800	< 165	1,122	1,800	852	2,050	2
Phenanthrene	85018	J 2,400	J 1,400	< 165	1,322	2,400	1,120	2,541	2
Pyrene	129000	J 930	< 1,650	< 165	548	930	541	1,725	1, 2
1–Methylnaphthalene	90120	140,000	150,000	17,000	102,333	150,000	74,070	182,997	2
2–Methylnaphthalene	91576	260,000	310,000	98,000	222,667	310,000	110,821	343,338	2
Naphthalene	91203	190,000	400,000	49,000	213,000	400,000	176,627	405,325	2

UNLEADED GASOLINE TANK SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl)phthalate	117817	370	< 50	< 50	157	370	185	358	
2,4–Dimethylphenol	105679	120	130	J 35	95	130	52	152	2
2–Methylphenol	95487	150	160	< 50	120	160	61	186	2
3/4–Methylphenol	NA	160	180	< 50	130	180	70	206	2
Indene	95136	390	J 100	J 26	172	390	192	381	
1–Methylnaphthalene	90120	190	J 100	210	167	210	59	230	2
2–Methylnaphthalene	91576	320	200	400	307	400	101	416	2
Naphthalene	91203	780	830	640	750	830	96	857	2

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	380.0	< 100.0	2,000	827	2,000	1,026	1,644	
Antimony	7440360	18.0	< 30.0	< 65.0	37.7	65.0	24.4	64.3	
Arsenic	7440382	35.0	240.0	17.0	97.3	240.0	123.9	232.2	
Cadmium	7440439	1.4	< 2.5	< 5.5	3.1	5.5	2.1	5.4	
Chromium	7440473	93.0	99.0	140.0	110.7	140.0	25.6	138.5	
Cobalt	7440484	20.0	< 25.0	< 55.0	33.3	55.0	18.9	53.9	
Copper	7440508	250.0	220.0	210.0	226.7	250.0	20.8	249.3	
Iron	7439896	340,000.0	350,000.0	550,000	413,333	550,000	118,462	542,325	
Lead	7439921	280.0	280.0	260.0	273.3	280.0	11.5	285.9	2
Manganese	7439965	1,300.0	1,500.0	2,400.0	1,733.3	2,400.0	585.9	2,371.4	
Mercury	7439976	0.10	0.27	0.16	0.18	0.27	0.09	0.27	
Molybdenum	7439987	14.0	< 32.5	< 70.0	38.8	70.0	28.5	69.9	
Nickel	7440020	550.0	< 20.0	4,900.0	1,823.3	4,900.0	2,677.6	4,738.9	
Vanadium	7440622	< 50.0	73.0	< 55.0	59.3	73.0	12.1	72.5	
Zinc	7440666	190.0	3,300.0	71.0	1,187.0	3,300.0	1,830.9	3,160.6	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6B–US–01	R8A–US–01	R16–US–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Iron	7439896	550.0	210.0	3.9	254.6	550.0	275.8	554.9	2
Lead	7439921	0.03	0.07	< 0.015	0.04	0.07	0.03	0.07	
Manganese	7439965	7.30	2.40	1.70	3.80	7.30	3.05	7.12	
Nickel	7440020	6.70	< 0.20	80.00	28.97	80.00	44.32	77.22	
Zinc	7440666	1.60	15.00	0.65	5.75	15.00	8.02	14.49	

Miscellaneous Characterization

	R6B–US–01	R8A–US–01	R16–US–01
Ignitability (oF)	84	75	No flash

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations

2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.

J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

ND Not Detected.

NA Not Applicable.

3.1.3 Clarified Slurry Oil Tank Sediment and Filter Solids - Residual 3

Clarified slurry oil is the bottom fraction from fluid catalytic cracking units, operated at 109 refineries. In 1992, U.S. refineries reported 297 dedicated clarified slurry oil (CSO) tanks with an average capacity of 45,000 barrels and 111 storage tanks with an average capacity of 55,000 barrels with commingled CSO and residual fuel oil.

3.1.3.1 Description

CSO is the lowest boiling fraction off the FCC's main fractionator (see Section 3.2 for FCC process description). The CSO contains some catalyst and catalyst fines (1-2 wt%). Some refineries have a slurry settler that removes up to 50% of these fines and returns them to the process. The top draw off the settler, CSO, is sent to a storage tank, where most of the remaining solid catalyst particles settle out, forming a sediment at the bottom of the tank. The tank sediment also contains rust. The CSO is sold as carbon black feedstock, residual fuel oil or bunker fuel. CSO sediment is generated in 3 ways: tank bottoms, filter solids, and during FCC unit cleanout\turnaround.

CSO tank bottoms are generated every 5-10 years during storage tank cleanout. As with crude tank sediment, many refineries use *in situ* and *ex situ* oil recovery techniques. Common *in situ* oil recovery techniques include hot distillate washing and steam stripping. These techniques allow entrapped oil to float to the top of the sediment for recovery prior to removal from the tank. *Ex situ* recovery methods, usually performed by a contractor at the tank site, include filtration, centrifuging, and settling. Separated oil is recycled back to the process or sent to the slop oil tanks; any water is sent to the WWTP. The solids are managed in a variety of ways including disposal at Subtitle C and D landfills and in land treatment units. It is not unusual for the sediment to be stabilized by using clay or kiln dust to soak up any remaining free oil.

Mixers are also installed on CSO tanks to reduce tank bottom buildup. Mixers keep the catalyst fines suspended in the CSO.

> 28% of the tanks that store CSO have mixers

Some refineries filter their CSO prior to storage. Cartridge filters are employed to remove catalyst fines which are entrained in the product. Filtered solids are generated once or twice a year, depending on product volume.

Every 2 to 3 years, the FCC is shutdown for turnaround. At this time, sediments may also be generated in the process equipment (e.g., hydroclone).

In 1992, approximately 1 percent of the volume of CSO sediment generated was reported to be managed as hazardous.

3.1.3.2 Generation and Management

The refineries reported generating approximately 24,010 MT of CSO sediment in 1992. Residuals were assigned to be "CSO sediment" if they were assigned a residual identification code of "FCC CSO tank sediment," "FCC CSO sediment, other than tank sediment," or "Other tank sediment/CSO [commingled]." These correspond to residual codes 01-D, 02-C, and 01-E, respectively, in Section VII.2 of the questionnaire. Process wastewaters, decantates, and recovered oils (e.g., from deoiling or dewatering operations) were eliminated from the analysis. These correspond to residual codes 09, 10, and 13 (new) in the questionnaire. Quality assurance was conducted by ensuring that all CSO tank sediments previously identified in the questionnaire (i.e., in Section V.D) were assigned in Section VII.2. Table 3.1.13 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.1.13. Generation Statistics for CSO Sediment, 1992

Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Discharge to onsite WWTP	1	0	250	250	250
Disposal offsite Subtitle D landfill	16	0	11,341	709	2,871*
Disposal onsite Subtitle D landfill	2	0	679	339.5	619
Disposal offsite Subtitle C landfill	9	1	3,564	396	2,278
Offsite land treatment	2	0	2,389	1,195	2,278
Onsite land treatment	4	1	2,906	726.5	2,520
Onsite industrial furnace	1	0	39	39	39
Transfer for use as fuel	3	0	1,850	617	1,724
Recovery/reuse onsite	2	2	581	290.5	381
Other recycling/onsite road material	2	0	411	205.5	314
Total CSO sediment	42	4	24,010	572	1,724

* Outlier quantities confirmed in §3007 survey.

[1] Reuse onsite includes recovery in catalytic cracker, coker, distillation unit or in asphalt production.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.1.13 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite land treatment (used for 12% of sediments)
- Offsite Subtitle D landfilling (47% of sediments)
- Onsite Subtitle D landfilling (3% of sediments)

An onsite monofill scenario was rejected because of the intermittent (every 10 years) generation frequency, which is not typical of wastes that tend to be monofilled.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.1.14.

Table 3.1.14. Selection of Risk Assessment Modeling Scenario: CSO Sediment

Waste	Basis for Consideration in Risk Assessment
Discharge to onsite WWTP	Not modeled. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be captured by existing hazardous waste listings and further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Disposal offsite Subtitle D landfill	Modeled
Disposal onsite Subtitle D landfill	Modeled
Disposal offsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Recovery/reuse onsite	Proposed excluded management practice
Offsite land treatment	Modeled
Onsite land treatment	Modeled
Transfer for use as fuel	Not modeled. Already regulated if characteristic.
Onsite industrial furnace	Not modeled. Minimal volume, unlikely to significantly impact emissions due to dilution. Already regulated if characteristic.
Other recycling/onsite road material	Similar application of much larger volume modeled under land treatment scenario.

The Agency evaluated whether it was necessary to model short-term on-site storage of CSO sediment prior to final management. Using the same logic described in the earlier discussion of the selection of management practices to be modeled for crude oil tank sediment, EPA determined that the potential for contaminant release and exposure at levels of concern was insignificant in comparison with the long-term risks associated with landfilling and land treatment. Therefore, on-site storage was not modeled in the Agency's risk assessment.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.1.15 provides a summary of the data for the targeted management practices used in the risk assessments for the CSO sediments. Appendix C summarizes §3007 data regarding runon/runoff controls used for these units.

As with crude oil tank sediment, many refineries conduct de-oiling of CSO tank sediment, both before and after removal from the storage tank. The Agency evaluated whether de-oiling has any impact on the risks associated with the disposed sediment. The Agency hypothesized that de-oiling might reduce toxicant concentrations for certain toxicant fractions (e.g., volatiles), although others could be concentrated (e.g., metals). Samples were collected of sediments with and without de-oiling after removal from the storage tanks (described further in Section 3.1.3.3). As discussed earlier in Section 3.1.1.2, after considering all of these factors, the Agency determined that differentiating between oily and de-oiled sediments was inappropriate. De-oiling reduces volume, which, if all other factors were held constant, would tend to reduce the risk modeled. The average de-oiled crude oil tank sediment volume is 514, while the average oily sediment volume is 384. De-oiled sediments are predominantly disposed of in offsite Subtitle D landfills (39%), disposed of in offsite Subtitle C landfills (30%), or sent to offsite land treatment (21%). Oily sediments are more likely to be disposed of in offsite Subtitle D landfills (53%), sent to offsite land treatment (22%), or transferred offsite for use as a fuel (14%).

Table 3.1.15. Management Practices Targeted for Risk Assessment							
CSO Sediment							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfill[3,4]	13	18	0	12,020	---	184.5	3,143
	Onsite Landfill Characteristics						
	Surface Area (acres)				0.4	30	250
	Remaining Capacity (thousand cu.yd.)				3.1	838	8,900
	Percent Remaining Capacity				2	40	80
	Total Capacity (thousand cu.yd.)				3.2	840	11,100
	Number of Strata in Completed Unit				0	5.5	11
	Depth Below Grade (ft)				8	29	50
	Height Above Grade (ft)				0	1.25	2.5
	# of Landfills: 2						
	Aquifer Information						
	Depth to Aquifer (ft)				39	62	85
	Distance to Private Well (ft)				8,970	8,970	8,970
	Population Using Private Well				-	-	-
	Distance to Public Well (ft)				58,000	58,000	58,000
	Population Using Public Well				1,500	1,500	1,500
	# of Aquifers: 2						
	Source: / Public / Private Unreported / 1 / 1 Uppermost / — / 1 Lowermost / 1 / --						
	Classification of Uppermost Aquifer: Not considered a potential source of drinking water (1) Current or potential source of drinking water (1)						

Table 3.1.15. Management Practices Targeted for Risk Assessment							
CSO Sediment							
Offsite Land Treatment Unit[3]	2	2	0	2,389	---	1,194.6	2,277.75
Onsite Land Treatment Unit[1,3]	5	4	1	2,905	—	190.95	2,520
	Characteristics						
	Surface Area (acres)				8.8	15	170
	Depth of Incorporation (in)				6	10	13.5
	Amount Applied (1992 MT)[2]				4	735	15,322
	Methods of Incorporation: Disking (7); Subsurface Injection (1); Springtooth Harrow (1)						
	# of Landfills: 9						
	Aquifer Information						
	Depth to Aquifer (ft)				12.5	16.75	265
	Distance to Private Well (ft)				1,000	6,200	25,000
	Population Using Private Well				300	300	300
	Distance to Public Well (ft)				6,500	13,200	25,000
	Population Using Public Well				—	—	—
	# of Aquifers: 8						
	Source:	Public		Private			
	Unreported	5		3			
	Uppermost	2		3			
	Lowermost	1		2			
	Combination	—		—			
	Classification of Uppermost Aquifer: Current or potential source of drinking water (3); Not considered a potential source of drinking water (5)						

[1] The number of onsite land treatment units characterized in Table 3.1.15 is greater than indicated in Table 3.1.13 which focuses only on volumes generated in 1992. Table 3.1.15 incorporates data from all onsite land treatment units receiving sediment in any year reported in the §3007 survey.
[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the CSO sediment and not just the sediment alone.
[3] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).
[4] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.1.3.3 Characterization

Since the industry varies management methods, the sampling profile reflects the fact that about half of the refineries do some sort of oil recovery prior to sediment disposal. As with most tank sediments, CSO sediment from tanks is available only during turnarounds, which occur every 5 to 10 years. CSO filters are generated more frequently, however, only one of the refineries selected for record sampling uses filters.

Two sources of residual characterization were developed during the industry study:

- Table 3.1.16 summarizes the physical properties of the CSO sediment as reported in Section VII.A of the §3007 survey.

Table 3.1.16. CSO Sediment Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	53	68	5	5	7.8
Reactive CN, ppm	29	92	0.02	26.4	250
Reactive S, ppm	35	86	1	91	250
Flash Point, °C	42	79	60	84.1	100
Oil and Grease, vol%	44	77	5	29.5	80
Total Organic Carbon, vol%	15	106	5	29	70
Viscosity, lb/ft-sec	3	116	0.14	666	1,000
Specific Gravity	41	80	1	1.4	2.1
BTU Content, BTU/lb	36	85	2,000	5,935	3,000
Aqueous Liquid, %	62	59	0	11.4	50
Organic Liquid, %	71	50	0	25.7	70
Solid, %	83	38	20	69.7	100
Particle >60 mm, %	6	115	0	16.7	100
Particle 1-60 mm, %	15	106	0	29.4	100
Particle 100 μm-1 mm, %	13	108	0	60.6	100
Particle 10-100 μm, %	13	108	0	28.5	45
Particle <10 μm, %	6	115	0	0	0
Mean Particle diameter, microns	8	112	25	612.5	800

- Due to the rarity of sediment generation, only 4 samples were available during record sampling. These included 1 oily tank sediment sample, 1 composite sample of both oily and de-oiled sediment, 1 de-oiled tank sediment sample, and 1 CSO filter. These sediments represent the various types of oil recovery typically used by the industry. Table 3.1.17 provides the sample location and description.

The 4 samples collected are believed to be representative of the sediment as generated. Table 3.1.18 provides a summary of the characterization data collected under this sampling effort. Only constituents detected in at least one sample are shown in this table. Of the CSO sediment samples collected, none exhibited the toxicity characteristic. The high aluminum content can be attributed to the FCC catalyst which makes up a majority of the solids in the sediment.

Table 3.1.17. CSO Sediment Record Sampling Locations

Sample #	Location	Description: Oil Recovery
R9-SO-01	Murphy, Superior, WI	CSO filter
R1B-SO-01	Marathon, Indianapolis, IN	CSO, classified as residual oil by refinery: oily and stabilized with cement kiln dust
R4-SO-01	Little America, Casper, WY	Tank sediment de-oiled through settling
R20-SO-01	Star Enterprise, Convent, LA	Centrifuged sediment

3.1.1.4 Source Reduction

In situ oil recovery techniques can greatly reduce the total volume of CSO tank sediment to be disposed. As discussed above, recovery methods include distillate washing, nonpetroleum solvent washing, water wash with surfactant, and steam stripping. This allows entrapped oil to float to the top and be recovered prior to removal from the tank. Separated oil is recycled back to the process or sent to the slop oil tanks, and the water phase is sent to the WWTP.

As with crude oil, tank bottom buildup may be reduced by installing mixers. Mixers keep the sediments or solids continuously in suspension so that they travel with the CSO. However, these solids may drop out later in the process, resulting in greater sediment generation at turnaround and possibly more frequent turnarounds.

Another method to reduce catalyst in the CSO is to install high-efficiency cyclones in the FCC reactor. This can shift the catalyst fines losses from the reactor to the regenerator where the fines can be collected in the electrostatic precipitator or wet gas scrubber (note that not all refineries are in States that require air pollution control on their FCCs). API estimated that 2 pounds of tank bottoms are prevented for every pound of catalyst exiting the regenerator instead of the reactor (see FCC unit process flow diagram) (API, 1991).

Some refineries have a slurry settler that removes up to 50% of the catalyst fines in the CSO and returns them to the process. By adding a settler to the FCC unit, sediment-forming solid catalyst particles can be greatly reduced.

Table 3.1.18. CSO Sediment Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.		R4–SO–01		R9–SO–01		R18–SO–01		R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	<	1,250	<	625	JB	1,400	JB	3,400	1,669	3,400	1,202	2,653	
Benzene	71432	<	1,250	J	1,200	<	1,250	<	2,500	1,200	1,200	NA	NA	1
n–Butylbenzene	104518	<	1,250		1,600		17,000		22,000	10,513	22,000	10,579	19,177	
sec–Butylbenzene	135988	<	1,250	<	625		2,600	J	3,000	1,869	3,000	1,117	2,784	
Ethylbenzene	100414	<	1,250		4,300		12,000		20,000	9,388	20,000	8,397	16,265	
Isopropylbenzene	98828	<	1,250	<	625	J	2,300	J	2,900	1,769	2,900	1,023	2,607	
p–Isopropyltoluene	99876	<	1,250	<	625		2,600	J	2,600	1,769	2,600	993	2,582	
Naphthalene	91203		2,900		11,000		19,000	E	140,000	43,225	140,000	64,851	96,338	
n–Propylbenzene	103651	<	1,250		2,700	<	1,250	<	2,500	1,925	2,700	784	2,567	
Toluene	108883		3,000		8,700		13,000		17,000	10,650	17,000	5,834	15,264	
1,2,4–Trimethylbenzene	95636		11,000		20,000		25,000	E	140,000	49,000	140,000	60,943	98,912	
1,3,5–Trimethylbenzene	108678		2,600		5,600		35,000		42,000	21,300	42,000	20,103	37,764	
o–Xylene	95476		3,000		7,500		27,000		40,000	19,375	40,000	17,250	33,503	
m,p–Xylenes	108383 / 106423		11,000		19,000		69,000		100,000	49,750	100,000	42,201	84,313	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R4–SO–01		R9–SO–01		R18–SO–01		R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	<	50	<	50	B	360	<	50	128	360	155	254	
Benzene	71432	<	50	J	84	<	50	<	50	59	84	17	72	
Methylene chloride	75092	<	50	<	50	JB	90	J	90	70	90	23	89	
Naphthalene	91203	<	50	<	50		140		200	110	200	73	170	
Toluene	108883	B	260		180		180	J	80	175	260	74	235	
1,2,4–Trimethylbenzene	95636	<	50	<	50		110		100	78	110	32	104	
o–Xylene	95476	B	110	<	50		110	J	60	83	110	32	109	
m,p–Xylene	108383 / 106423	B	250		100		250		160	190	250	73	250	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R4–SO–01		R9–SO–01		R18–SO–01		R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	<	61,875		46,000		53,000		160,000	80,219	160,000	53,583	124,103	
Anthracene	120127	<	61,875		77,000	J	32,000		86,000	64,219	86,000	23,874	83,807	
Benz(a)anthracene	56553		380,000		390,000	<	20,625	<	41,250	202,969	390,000	199,200	366,113	
Benzofluoranthene (total)	NA	J	110,000		110,000	J	27,000	J	60,000	76,750	110,000	40,669	110,074	2
Benzo(g,h,i)perylene	191242	J	90,000		100,000	J	23,000	J	63,000	69,000	100,000	34,419	97,189	
Benzo(a)pyrene	50328		230,000		170,000		52,000	J	76,000	132,000	230,000	82,833	199,840	
Carbazole	86748	<	123,750		87,000	<	41,250	J	67,000	65,083	87,000	22,935	90,057	1, 2
Chrysene	218019		700,000		860,000		170,000		220,000	487,500	860,000	344,813	769,736	
Dibenz(a,h)anthracene	53703	<	61,875		49,000	<	20,625	<	41,250	36,958	49,000	14,666	52,926	1, 2
Dibenzofuran	132649	<	61,875		21,000	J	31,000	J	37,000	29,667	37,000	8,083	38,468	1, 2
7,12–Dimethylbenz(a)anthracene	57976	<	61,875		1,200,000	<	20,625	<	41,250	330,938	1,200,000	579,620	805,646	
Fluoranthene	206440	J	43,000		130,000	J	28,000	J	49,000	62,500	130,000	45,858	100,056	
Fluorene	86737	<	61,875		110,000		74,000		200,000	111,469	200,000	62,459	162,623	
Indeno(1,2,3–cd)pyrene	193395	<	61,875		26,000	<	20,625	<	41,250	23,313	26,000	3,801	31,565	1, 2
3–Methylcholanthrene	56495	<	61,875	<	20,625	J	27,000	<	41,250	23,813	27,000	4,508	33,624	1, 2
2–Methylchrysene	3351324		660,000		460,000		160,000		230,000	382,500	660,000	221,566	563,963	
1–Methylnaphthalene	90120	J	140,000		290,000		570,000		2,200,000	800,000	2,200,000	950,193	1,578,208	
2–Methylnaphthalene	91576		190,000		420,000		960,000	E	3,600,000	1,292,500	3,600,000	1,571,622	2,579,822	
2–Methylphenol	95487	J	32,000	<	20,625	<	20,625	<	41,250	24,417	32,000	6,567	31,566	1
3/4–Methylphenol (total)	NA	J	41,000	<	20,625	<	20,625	<	41,250	27,417	41,000	11,764	40,226	1
Naphthalene	91203	J	82,000		88,000		160,000		360,000	172,500	360,000	134,862	282,952	
Phenanthrene	85018		200,000		1,000,000		320,000		860,000	550,000	1,000,000	362,767	847,106	
Phenol	108952	J	93,000	J	7,600	<	20,625	<	41,250	40,619	93,000	37,589	71,367	
Pyrene	129000		480,000		610,000		210,000		550,000	462,500	610,000	176,517	607,066	

CSO SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R4–SO–01	R9–SO–01	R18–SO–01	R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2–ethylhexyl)phthalate	117817	< 50	JB 21	< 50	< 50	21	21	NA	NA	1
Di–n–butyl phthalate	84742	< 50	J 39	< 50	< 50	39	39	NA	NA	1
2,4–Dimethylphenol	105679	< 50	< 50	< 50	J 91	60	91	21	77	
1–Methylnaphthalene	90120	< 50	JB 17	140	< 50	64	140	53	108	
2–Methylnaphthalene	91576	J 27	J 22	210	J 14	68	210	95	148	
2–Methylphenol	95487	< 50	< 50	< 50	J 86	59	86	18	74	
3,4–Methylphenol (total)	NA	< 50	< 50	J 32	J 76	52	76	18	67	
Naphthalene	91203	J 32	J 23	170	< 50	69	170	68	125	
Phenanthrene	85018	< 50	J 12	< 50	< 50	12	12	NA	NA	1
Phenol	108952	< 50	< 50	JB 83	120	78	120	33	103	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R4–SO–01	R9–SO–01	R18–SO–01	R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	59,000	22,000	23,000	45,000	37,250	59,000	17,970	51,987	
Antimony	7440360	< 6.0	940.0	< 6.0	< 6.0	239.5	940.0	467.0	622.0	
Arsenic	7440382	< 5.0	4.7	< 5.0	< 1.0	2.9	4.7	2.6	6.5	1, 2
Barium	7440393	150.0	48.0	170.0	55.0	105.9	170.0	63.2	157.5	
Beryllium	7440417	1.2	< 0.6	< 0.5	< 0.6	0.7	1.2	0.3	1.0	
Calcium	7440702	1,100.0	< 500.0	100,000.0	< 500.0	25,525.0	100,000.0	49,650.6	66,189.0	
Chromium	7440473	25.0	8.4	34.0	26.0	23.4	34.0	10.7	32.2	
Copper	7440508	20.0	7.8	53.0	13.0	23.5	53.0	20.3	40.1	
Iron	7439896	8,000.0	2,400.0	11,000.0	3,300.0	6,175.0	11,000.0	4,046.7	9,489.3	
Lead	7439921	23.0	17.0	47.0	17.0	26.0	47.0	14.3	37.7	
Magnesium	7439954	< 500.0	< 500.0	8,000.0	< 500.0	2,375.0	8,000.0	3,750.0	5,446.3	
Manganese	7439965	30.0	15.0	240.0	22.0	76.8	240.0	109.0	166.0	
Mercury	7439976	0.11	< 0.05	< 0.05	< 0.05	0.07	0.11	0.03	0.09	
Molybdenum	7439987	< 6.5	< 6.5	< 6.5	160.0	44.9	160.0	76.7	107.7	
Nickel	7440020	300.0	120.0	62.0	160.0	160.5	300.0	101.3	243.5	
Potassium	7440097	< 500.0	< 500.0	11,000.0	< 500.0	3,125.0	11,000.0	5,250.0	7,424.8	
Selenium	7782492	< 0.6	< 0.5	5.1	< 0.6	1.7	5.1	2.3	3.5	
Sodium	7440235	5,200.0	1,700.0	1,600.0	2,000.0	2,625.0	5,200.0	1,725.1	4,037.8	
Thallium	7440280	< 1.0	< 1.0	2.5	< 1.0	1.4	2.5	0.7	2.0	
Vanadium	7440622	430.0	280.0	91.0	310.0	277.9	430.0	140.4	392.7	
Zinc	7440666	100.0	24.0	64.0	32.0	55.0	100.0	34.6	83.4	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R4–SO–01	R9–SO–01	R18–SO–01	R20–SO–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	< 1.00	< 1.00	7.00	2.70	2.93	7.00	2.83	5.24	
Calcium	7440702	< 25.00	< 25.00	4,500.00	< 25.00	1,143.75	4,500.00	2,237.50	2,978.26	
Iron	7439896	< 0.50	< 0.50	1.10	2.00	1.03	2.00	0.71	1.61	
Magnesium	7439954	< 25.00	< 25.00	240.00	< 25.00	78.75	240.00	107.50	166.79	
Manganese	7439965	< 0.08	< 0.08	4.40	0.27	1.21	4.40	2.13	2.95	
Nickel	7440020	< 0.20	< 0.20	< 0.20	0.52	0.28	0.52	0.16	0.41	
Potassium	7440097	< 25.00	< 25.00	360.00	< 25.00	108.75	360.00	167.50	245.93	
Zinc	7440666	0.28	< 0.10	0.37	< 0.10	0.21	0.37	0.13	0.32	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected
NA Not Applicable

3.2 CATALYTIC CRACKING

3.2.1 Process Description

Catalytic cracking is a process for the conversion of straight-run atmospheric gas oil, vacuum gas oils, and heavy stocks recovered from other operations into high-octane gasoline, light fuel oils and olefin-rich light gases. Available catalytic cracking technologies include fluid catalytic cracking, residual catalytic cracking, and Thermofor catalytic cracking. Because catalytic cracking increases the gasoline yield from crude oil, over 60% of the refineries in the United States have at least one of these units.

> FCC is an effective process for increasing the yield of gasoline from crude oil

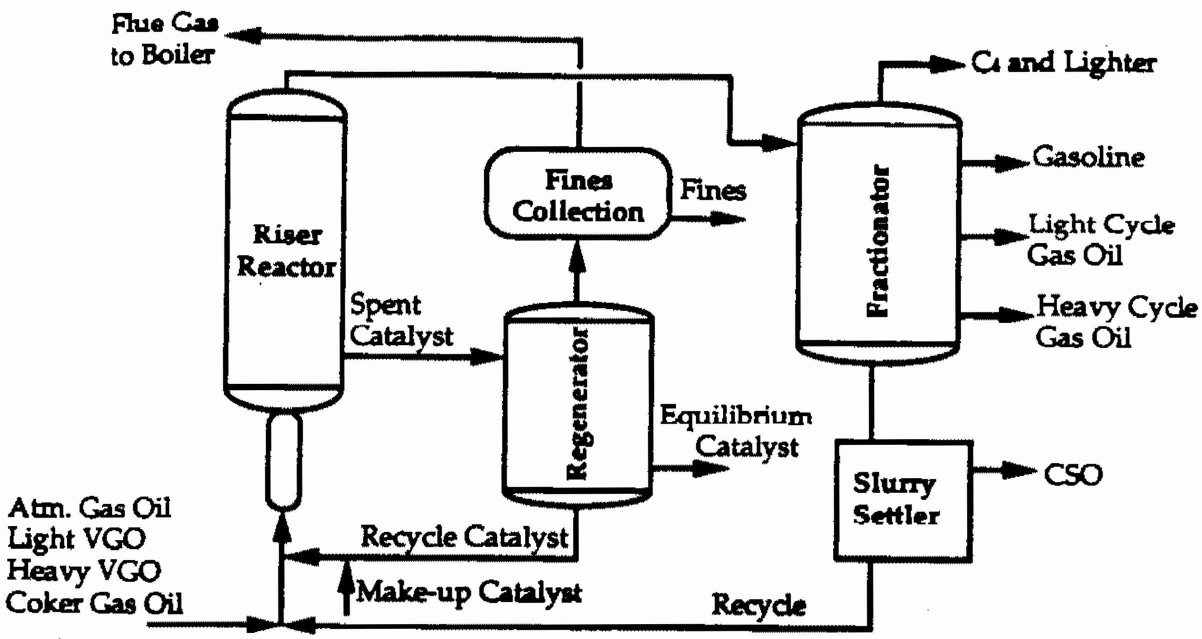
Fluid catalytic cracking (FCC) is by far the most widely used by industry (95% of all catalytic cracking units in the U.S.) and will be the primary focus of this discussion. FCC capacities range from 2,400 to 120,000 barrels per stream day. The silica-alumina catalyst has a small particle size (average size 51 to 65 μm) and moves through the reactor as a fluid. Figure 3-2-1 provides a generic process flow diagram for fluid catalytic cracking. In the FCC process, light and heavy vacuum gas oil and a mixture of middle to heavy petroleum fractions are preheated and then contacted with hot FCC catalyst. The reactor's temperature is 850° to 950°F and its pressure is between 12 to 50 psig (McKetta, 1992). The oil vaporizes and forms a fluidized mixture with the catalyst particles and is literally blown around the large reactor. The oil cracks forming lighter hydrocarbons as it rises through the reactor. The oil and catalyst are separated by cyclones at the top of the reactor, and the cracked products are recovered in the main fractionator.

The fractionator separates the cracked hydrocarbons into products. The products are generally light gases (butanes and lighter), cat cracked gasoline, light and heavy gas oils, and CSO. See Section 3.1.3 for further description of CSO generation.

During the cracking process, coke deposits on the catalyst and renders it inactive. The coke is burned off the catalyst in the regenerator. The regenerator operates at a higher temperature (1100° to 1300°F) than the reactor which allows the coke to be burned off. The bulk of the regenerated catalyst is recycled back to the reactor. However, because the catalyst loses some activity over time due to deposition of metals (e.g., vanadium and nickel) and neutralization of active acid sites (e.g, sodium and sulfate), a slip stream of catalyst is removed after regeneration and replaced with fresh catalyst. This slip stream of catalyst, typically 1% of the catalyst inventory, is called equilibrium catalyst, a residual of concern. Catalyst losses can also be attributed to fines entrained in the regenerator off-gas or flue gas and in the CSO.

Depending on local air pollution control standards, catalyst fines from the regenerator flue gas may be removed in an electrostatic precipitator or a wet gas scrubber, or can be sent to the stack. The collected catalyst fines are a residual of concern.

Figure 3.2.1. Fluid Catalytic Cracking Process Flow Diagram



As mentioned above, other process variations include residual catalytic cracking (RCC) and Thermofor catalytic cracking (TCC). The RCC is basically the same configuration as the FCC unit varying only in the feed. The feed is a mixture of fractions from the vacuum unit. This heavier grade feed has a higher metals content which causes the catalyst to lose its activity more quickly. Larger reactors are used to compensate for the metals loading.

In 1992, four refineries had TCC units with capacities ranging from 4,500 to 17,000 barrels per stream day. The TCC unit is a moving-bed cracking unit. In the moving bed process, the catalyst (a zeolitic catalyst) is pelletized into about 1/8 inch diameter beads. These beads flow by gravity from the top of the unit down through the reactor which operates at about 10 psig and 850° to 925°F (McKetta, 1992). The oil is injected at the top of the reactor and flows concurrently with the bead catalyst to the bottom of the reactor where product vapors are collected in underflow weir channels and are ducted to the fractionator. The catalyst then flows down to the regenerator or kiln. In the regenerator, air is introduced and the temperature is raised to about 1150° to 1250°F to burn off the coke which formed on the catalyst during the cracking process. Bucket elevators or pneumatic lifts are used to carry the catalyst from the bottom of the regenerator back to the top of the reactor.

3.2.2 FCC Equilibrium Catalyst - Residual 4

3.2.2.1 Description

As discussed above, heavy polyaromatic coke and carbon deposit on the silica-alumina catalyst during the cracking process causing it to lose its activity and become spent. These deposits are removed by burning the coked catalyst in the regenerator to reestablish activity prior to its recycle to the reactor. Metals, such as vanadium and nickel, from the crude oil also deposit on the catalyst, reducing activity. To control metal levels on the catalyst, equilibrium catalyst is drawn from the regenerator frequently (about once a week) and replaced with fresh catalyst.

Factors contributing to the degradation of the catalyst include high temperature, impurities in the fresh catalyst, impurities in the hydrocarbon feed, and time. Residual impurities in the fresh manufactured catalyst are principally sodium and sulfate. Impurities from the feed are sodium, nickel, vanadium, iron and copper. Sodium acts to neutralize active acid sites and aids in matrix degradation. Deposited metals effectively act as catalyst poisons. Metals levels on equilibrium catalyst reflect the metals content of the feeds being processed; typical ranges are 200 to 1,200 ppm vanadium, 150 to 500 ppm nickel, and 5 to 45 ppm copper. Sodium levels are in the range of 0.25 to 0.8 wt% (as NaO_2) (McKetta, 1992).

The equilibrium catalyst from the regenerator is placed in a catalyst hopper where it is cooled and stored prior to final management. Equilibrium catalyst from one refinery's FCC may be used at another refinery where the FCC unit requires a catalyst with a lower activity level.

Although this is a high-volume stream, less than 3 percent of its volume is currently managed as hazardous. Some refineries manage their FCC catalyst and fines in onsite dedicated catalyst monofills.

The catalyst in the TCC unit is a zeolitic bead-type catalyst that is removed and replaced only during turnaround. The catalyst makeup, frequency of generation, and process design are all different from the FCC process. In addition, the TCC process is much less common than the FCC and RCC processes. Therefore, the catalyst in the TCC unit was not considered to be within the scope of this study.

3.2.2.2 Generation and Management

The §3007 questionnaire responses indicated 124,061 MT of equilibrium catalyst were generated in 1992. Residuals were assigned to be "FCC catalyst" if they were assigned a residual identification code of "spent solid catalyst" and were generated from a process identified as an FCC unit. This corresponds to residual code 03-A in Section VII.2 of the questionnaire and process code 04-A in Section IV-1.C of the questionnaire. Except for the RCC, other catalytic cracking units were omitted from this designation. In this industry study, equilibrium catalyst was the largest volume of spent catalyst examined. Table 3.2.1 provides a description of the total quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.2.1. Generation Statistics for FCC Equilibrium Catalyst					
Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Disposal offsite Subtitle D landfill	35	0	23,326.5	666	1,575
Disposal onsite Subtitle D landfill	11	0	2,894	263	1,125
Disposal offsite Subtitle C landfill	3	0	155	52	140
Disposal onsite Subtitle C landfill	4	0	3,982	995	3,072
Offsite land treatment	3	0	713	238	446
Onsite land treatment	2	0	559.6	280	512
Onsite reuse	8	2	4,051	506	2,388
Other reuse/cement plant[2]	40	0	55,901	1,397.5	4,811
Transfer to offsite entity[1]	5	0	1,740	348	1,196
Transfer metal catalyst for reclamation	4	0	5,922	1480	2,627.6
Transfer to another petroleum refinery	62	1	24,817	400	890
Total FCC catalyst	178	3	124,061	697	1,575

[1] Offsite entities include alumina manufacturer and steel industry.

[2] Includes quantities reported to be transfered for ingredient in products placed on land.

Plausible management scenarios were chosen by EPA on which to perform risk assessment modeling. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.2.1 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment.

The selected management practice is:

- An onsite monofill will be used as the worst-case plausible mismanagement. Because the volumes and generation rates are sufficient, onsite monofills are used by industry and plausible large volumes can go into a monofill. Refineries reported 26,221 MT (about 21 percent) of catalyst were disposed in Subtitle D landfills.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.2.2. The management unit characterization data were provided in the §3007 survey. Table 3.2.3 provides a summary of the management unit characteristics and aquifer information.

The Agency did not model storage of FCC catalysts and fines. FCC catalysts and fines are typically managed in pneumatic containers and hoppers prior to final management due to their particle sizes and the large volumes handled. These storage vessels are designed to minimize dust emissions and control losses. The Agency, however, did model potential air releases in the modeled monofill scenario for FCC residuals. Thus, interim storage was not modeled because of the nature of the storage vessels typically used and the consideration of air pathway releases during long-term final management.

3.2.2.3 Characterization

The category of "catalyst and fines from catalytic cracking" as defined in the EDF consent decree includes the subcategories of "equilibrium catalyst" and "fines". These subcategories were chosen because these two residuals are generated at different points in the process and because the Agency hypothesized that the different particle sizes of catalyst and fines might result in different risk results. See Section 3.2.3 for a description of fines from catalytic cracking.

Two sources of residual characterization were developed during the industry study:

- Table 3.2.4 summarizes the physical properties of the catalyst as reported in Section VII.A of the §3007 survey.
- The two equilibrium catalyst samples were collected and analyzed by EPA. The samples were collected from the catalyst hoppers during normal operating conditions. Table 3.2.5 provides the location and description of the samples.

These samples are believed to be representative because they were taken from units accepting various types of crude feeds neither of which were pretreated (hydrotreated). Table 3.2.6 provides a summary of the characterization data. Only constituents detected in at least one sample are shown in this table. As shown in the data, none of the FCC catalyst samples exhibited the toxicity characteristic even though heavy metals are present. High aluminum concentrations can be attributed to the silica-alumina catalyst. Because of the severe operating conditions of the unit, the spent catalyst has a very low organic content.

Table 3.2.2. Selection of Risk Assessment Modeling Scenario: FCC Equilibrium Catalyst	
Waste	**Basis for Consideration in Risk Assessment**
Disposal offsite Subtitle D landfill	Monofill scenario was assumed to pose greatest potential risk because the residual is not mixed or diluted with other materials in an unlined monofill.
Disposal onsite Subtitle D landfill	Modeled as a monofill as worst case bounding estimate.
Disposal offsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite land treatment	Monofill scenario was assumed to pose greatest potential risk
Onsite land treatment	Monofill scenario was assumed to pose greatest potential risk
Onsite reuse	Excluded management practice
Other reuse/cement plant	Not modeled. Assumed small percentage of feed to cement kiln with very low levels of constituents of concern. Cement would tend to immobilize any trace metals.
Transfer to offsite entity[1]	Not modeled, assumed to be used as a raw material substitute, excluded management practice
Transfer metal catalyst for reclamation	Sent to exempt recycling
Transfer to another petroleum refinery	Not modeled, excluded management practice
Other storage	Not modeled, not final management

[1] Offsite entities include alumina manufacturer and steel industry.

Table 3.2.3. Management Practices Targeted for Risk Assessment							
FCC Equilibrium Catalyst							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite Subtitle D Landfills	—	11	0	2,894.2	—	36.5	1,125
Offsite Subtitle D Landfills	—	35	0	23,326.5	—	235	1,575
Onsite and Offsite Subtitle D Landfills[1]	31	46	0	26,221	—	197	1,693
	Onsite Landfill Characteristics						
	Surface Area (acres)				1.25	5.9	33
	Remaining Capacity (1000 cu.yd.)				3.025	24.45	6,500
	Percent Remaining Capacity				0.48	5	34.5
	Total Capacity (1000 cu.yd.)				12.1	75.325	10,498
	Number of Strata in Completed Unit				0	3	8,030
	Depth Below Grade (ft)				0.5	6	32.5
	Height Above Grade (ft)				0	7	72
	# of Landfills: 10						
	Aquifer Information						
	Depth to Aquifer (ft)				14	34.5	232.5
	Distance to Private Well (ft)				1,000	8,970	37,500
	Population Using Private Well				1	1	1
	Distance to Public Well (ft)				5,000	9,850	58,000
	Population Using Public Well				1,500	1,750	2,000
	# of Aquifers: 10						
	Source: / Unreported / Uppermost / Lowermost / Combination	Public: / 4 / 4 / 1 / —	Private: / 4 / 2 / 3 / —				
	Classification of Uppermost Aquifer: Current or potential source of drinking water (4); Not considered a potential source of drinking water (6)						

[1] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).

Table 3.2.4. FCC Equilibrium Catalyst Physical Properties					
Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	58	85	4.3	5.9	8
Reactive CN, ppm	42	101	0	19.2	10
Reactive S, ppm	45	98	0	19.1	67.5
Flash Point, °C	41	102	60	106.3	140
Oil and Grease, vol%	36	107	0	0.21	1
Total Organic Carbon, vol%	36	107	0	0.2	1
Specific Gravity	66	77	0.85	1.56	2.25
BTU Content, BTU/lb	15	128	0	776.7	1,000
Aqueous Liquid, %	84	59	0	0.24	0
Organic Liquid, %	83	60	0	0.05	0
Solid, %	126	17	100	99.4	100
Particle >60 mm, %	48	95	0	0.28	0
Particle 1-60 mm, %	48	95	0	8.6	4.5
Particle 100 μm-1 mm, %	55	88	0	30.4	100
Particle 10-100 μm, %	71	72	20	71.3	100
Particle <10 μm, %	61	82	0	6.8	15
Mean Particle diameter, microns	60	81	50	74	84

Table 3.2.5. FCC Equilibrium Catalyst Record Sampling Locations		
Sample Number	Location	Description
R4-FC-01	Little America, Casper, WY	FCC equilibrium catalyst from hopper
R6-FC-01	Shell, Norco, LA	FCC equilibrium catalyst off the regenerator

3.2.2.4 <u>Source Reduction</u>

Source reduction techniques are very difficult to formulate due to the limited number of inputs to the system. The FCC unit inputs are heavy hydrocarbons and catalyst, neither of which can be reduced, substituted or eliminated. However, by employing process efficiency modifications and/or reuse procedures, spent catalyst can be diverted from landfilling.

One refinery reported in the §3007 survey that caked FCC catalyst generated during turnaround was eliminated due to equipment and process changes.

A Peruvian FCC unit's operations were improved by increasing the regenerator's catalyst level. This increase resulted in lower stack losses, an improved temperature profile, increased catalyst activity and a lower catalyst consumption rate. (HC Processing, 11/93)

> Peruvian refiner saves over $131,000 per year in catalyst purchases

Hydrotreating FCC feed helps to remove metals and sulfur compounds from the feed. This can extend the life of the FCC equilibrium catalyst, which decreases the volume of spent catalyst generated.

One common example of reuse is the use of equilibrium catalyst from one refinery's FCC at another refinery where the FCC unit requires catalyst with a lower activity level. In 1992, 50,000 MT of spent catalyst were used as a feedstock in the production of cement.

Table 3.2.6. FCC Equilibrium Catalyst Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.	R4–FC–01	R6–FC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Ethylbenzene	100414	6,400	< 570	3,485	6,400	4,122	12,457	2
n–Propylbenzene	103651	2,200	< 570	1,385	2,200	1,153	3,894	2
Toluene	108883	17,000	< 570	8,785	17,000	11,616	34,071	2
1,2,4–Trimethylbenzene	95636	13,000	1,300	7,150	13,000	8,273	25,156	2
1,3,5–Trimethylbenzene	108678	5,100	< 570	2,835	5,100	3,203	9,807	2
o–Xylene	95476	11,000	< 570	5,785	11,000	7,375	21,837	2
m,p–Xylenes	108383 / 106423	35,000	< 570	17,785	35,000	24,346	70,773	2
Methyl ethyl ketone	78933	1,400	< 570	985	1,400	587	2,262	2
Naphthalene	91203	< 625	3,000	1,813	3,000	1,679	5,466	2

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R4–FC–01	R6–FC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	100	< 50	75	100	35	152	2
Toluene	108883	B 160	< 50	105	160	78	274	2
m,p–Xylenes	108383 / 106423	B 150	< 50	100	150	71	254	2
Methyl ethyl ketone	78933	150	< 50	100	150	71	254	2

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R4–FC–01	R6–FC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
1–Methylnaphthalene	90120	J 510	< 165	338	510	244	868	2
2–Methylnaphthalene	91576	870	< 165	518	870	499	1,602	2
Naphthalene	91203	670	< 165	418	670	357	1,195	2
Di–n–butyl phthalate	84742	< 165	1,000	583	1,000	590	1,868	2

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R4–FC–01	R6–FC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis (2–ethylhexyl)phthalate	117817	JB 23	J 15	19	23	6	31	2

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R4–FC–01	R6–FC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	89,000.0	31,000.0	60,000.0	89,000.0	41,012.2	149,282.0	2
Arsenic	7440382	< 1.0	2.5	1.8	2.5	1.1	4.1	2
Barium	7440393	190.0	< 20.0	105.0	190.0	120.2	366.6	2
Beryllium	7440417	2.7	1.7	2.2	2.7	0.7	3.7	2
Calcium	7440702	1,700.0	< 500.0	1,100.0	1,700.0	848.5	2,946.8	2
Chromium	7440473	17.0	4.0	10.5	17.0	9.2	30.5	2
Cobalt	7440484	< 5.0	18.0	11.5	18.0	9.2	31.5	2
Copper	7440508	19.0	13.0	16.0	19.0	4.2	25.2	2
Iron	7439896	4,800.0	1,000.0	2,900.0	4,800.0	2,687.0	8,748.2	2
Lead	7439921	42.0	11.0	26.5	42.0	21.9	74.2	2
Manganese	7439965	32.0	< 1.5	16.8	32.0	21.6	63.7	2
Nickel	7440020	330.0	91.0	210.5	330.0	169.0	578.3	2
Sodium	7440235	9,800.0	1,900.0	5,850.0	9,800.0	5,586.1	18,008.1	2
Vanadium	7440622	1,200.0	720.0	960.0	1,200.0	339.4	1,698.7	2
Zinc	7440666	68.0	9.3	38.7	68.0	41.5	129.0	2

FCC EQUILIBRIUM CATALYST

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R4-FC-01		R6-FC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Antimony	7440360	<	0.30		2.00	1.15	2.00	1.20	3.77	2
Iron	7439896	<	0.50		1.30	0.90	1.30	0.57	2.13	2
Nickel	7440020	<	0.20		1.10	0.65	1.10	0.64	2.04	2
Vanadium	7440622		9.50		0.85	5.18	9.50	6.12	13.49	2
Zinc	7440666		0.25	<	0.10	0.18	0.25	0.11	0.41	2

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.2.3 FCC Catalyst Fines - Residual 5

3.2.3.1 Description

Fluid catalytic cracking is the only catalytic cracking process that generates a residual of catalyst fines (RCCs also produce catalysts fines, however the RCC process is identical to the FCC process only processing heavier feeds). In the FCC process, the flue gas off the regenerator will likely have any of a number of optional units associated with it for air pollution control. The flue gas is composed of catalyst fines, nitrogen from the air used for combustion, the products of coke combustion (the oxides of carbon, sulfur, nitrogen, and water vapor), and trace quantities of other compounds (Meyers, 1986). Flue gas is directed through cyclone separators to minimize catalyst entrainment prior to discharge from the regenerator. The flue gas exits the regenerator at high temperature, approximately 700° to 780°C, and at pressure of about 30 psig. Depending on local air pollution control standards, the remaining catalyst fines may be removed in an electrostatic precipitator or a wet gas scrubber, or can be sent directly to the stack.

In electrostatic precipitators, catalyst fines are collected by using the mutual attraction between particles of one electrical charge and a collecting electrode of opposite polarity. Using high-voltage electrodes, the flue gas is ionized and the catalyst fines in the gas become charged. The charged fines then migrate to the plate electrodes, where fines collection occurs. The deposited fines are usually removed from the electrodes by rapping or vibration. With relatively weak electrical attraction between the fines adjacent to the plate and the plate itself, the fines fall by gravity into a collection hopper (Wark and Warner, 1981).

In wet gas scrubber systems, the flue gas and any entrained catalyst are scrubbed using a circulating water system. Caustic is added to the water to neutralize the SO_2 and NH_3 scrubbed out of the flue gas. Some refineries use spent caustic from liquid treating operations in their FCC off-gas scrubbers. The catalyst fines settle out of the water in scrubber ponds or are sent to a dewatering system. The catalyst is removed from the ponds as needed.

Although this is a high-volume stream, less than 2 percent of its volume is currently managed as hazardous. Some refineries manage their FCC catalyst and fines in an onsite dedicated catalyst monofill.

3.2.3.2 Generation and Management

The §3007 questionnaire responses indicated that 67,816 MT of catalyst fines were generated in 1992. Residuals were assigned to be "FCC fines" if they were assigned a residual identification code of "solid catalyst fines" and were generated from a process identified as an FCC unit. This corresponds to residual code 03-B in Section VII.2 of the questionnaire and process code 04-A in Section IV-1.C of the questionnaire. Except for the RCC, other catalytic cracking units were omitted from this designation. Table 3.2.7

provides a description of the total quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.2.7. Generation Statistics for FCC Catalyst Fines					
Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Disposal offsite Subtitle D landfill	44	1	32,819	746	1,250
Disposal onsite Subtitle D landfill	11	0	8,501	773	1,718
Disposal offsite Subtitle C landfill	4	0	763	190	550
Disposal onsite Subtitle C landfill	2	0	11.4	5.7	6.4
Offsite land treatment	2	0	419	210	416
Disposal/storage in surface impoundments[1]	4	0	7,096	1,774	5,309
Other disposal onsite/cap for landfarm	2	0	2,930	1465	1,630
Other disposal onsite/fill material	1	0	1,633	1,633	1,633
Other disposal onsite/vent to atmosphere	8	1	1,640	205	421.4
Recovery onsite in FCC	1	0	250	250	250
Other reuse/cement plant	19	0	10,048	529	1,460
Transfer for use in products placed on the land	2	0	1352	676	698
Transfer to another petroleum refinery	1	0	91	91	91
Settling	2	0	263	131.5	263
Total FCC fines	103	5	67,816	658	1,627

[1] Five facilities with 6 surface impoundments were reported in the §3007 survey (for all generating years). Two are permitted as SWMUs, five are used for interim or final management of scrubber fines.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.2.7 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment.

The selected management practices are:

- An onsite monofill will be used as the worst-case plausible mismanagement. Because the volumes and generation rates are sufficient, onsite monofills are used by industry and plausible large volumes can go into a monofill. Refineries reported 41,320 MT (about 61 percent) of catalyst fines were disposed in Subtitle D landfills.

- While it appears to be a relative rare practice, the Agency also modeled disposal in surface impoundments to confirm that the scenario was not of concern.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.2.8.

The Agency did not model storage of FCC catalysts and fines. FCC catalysts and fines are typically managed in pneumatic containers and hoppers prior to final management due to their particle sizes and the large volumes handled. These storage vessels are designed to minimize dust emissions and control losses. The Agency, however, did model potential air releases in the modeled monofill scenario for FCC residuals. Thus, interim storage was not modeled because of the nature of the storage vessels typically used and the consideration of air pathway releases during long-term final management.

Management unit characteristics were reported in the §3007 questionnaire. Table 3.2.9 provides the management unit information for the FCC fines. Table 3.2.10 provides the management unit information for the FCC catalyst and fines combined.

Table 3.2.8. Selection of Risk Assessment Modeling Scenario: FCC Catalyst Fines	
Management	**Basis for Consideration in Risk Assessment**
Disposal offsite Subtitle D landfill	Not modeled, monofill scenario was assumed to pose greatest potential risk because the residual is not mixed with or diluted with other materials in an unlined monofill
Disposal onsite Subtitle D landfill	Modeled as a monofill
Disposal offsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite land treatment	Not modeled, monofill scenario was assumed to pose greatest potential risk
Disposal/storage in surface impoundments	Modeled
Other disposal onsite[1]	Covered by landfill scenario
Recovery onsite in FCC	Not modeled, assumed closed loop recycling
Other reuse/cement plant	Not modeled, assumed small percentage of feed to cement kiln with very low levels of constituents of concern. Cement would tend to immobilize any trace metals present.
Transfer for use in products placed on the land	Not modeled, assumed to be used in cement manufacture, see above
Transfer to another petroleum refinery	Not modeled, exempt management practice
Settling	Not modeled, not a final management practice

[1] Other onsite disposal includes cap for landfarm, fill material, and vent to atmosphere.

Table 3.2.9. Management Practices Targeted for Risk Assessment							
FCC Catalyst Fines							
Parameters	# of Fac.	# of RC	# RC w/ Unreported Volume	Total Volume (MT)	10th % Volume (MT)	50th % Volume (MT)	90th % Volume (MT)
Onsite Subtitle D Landfills	—	11	0	8,501.2	—	332	1,718.2
Offsite Subtitle D Landfills	—	44	1	32,819.1	—	331	1,250
Onsite and Offsite Subtitle D Landfills[1]	40	55	1	41,320	—	414	2,753.6
	Onsite Landfill Characteristics						
	Surface Area (acres)				1	7	50
	Remaining Capacity (1000 cu.yd.)				3.63	24.45	8,900
	Percent Remaining Capacity				0.5	5	25
	Total Capacity (1000 cu.yd.)				15	75.325	10,200
	Number of Strata in Completed Unit				0	1	400
	Depth Below Grade (ft)				1	5	15
	Height Above Grade (ft)				0	7	25
	# of Landfills: 11						
	Aquifer Information						
	Depth to Aquifer (ft)				7	29.5	207
	Distance to Private Well (ft)				5,000	8,985	26,800
	Population Using Private Well				3	3	3
	Distance to Public Well (ft)				5,000	13,200	58,000
	Population Using Private Well				250	1,750	2,000
	# of Aquifers: 10						
	Source: Public Private Unreported 5 2 Uppermost 2 1 Lowermost 1 5						
	Classification of Uppermost Aquifer Current or potential source of drinking water (3) Not considered a potential source of drinking water (7)						

[1] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).

Table 3.2.10. Management Practices Targeted for Risk Assessment

FCC Catalyst and Fines

Parameters	# of Fac.	# of RC	# RC w/ Unreported Volume	Total Volume (MT)	10th % Volume (MT)	50th % Volume (MT)	90th % Volume (MT)
Onsite Subtitle D Landfills[2]	11	22	0	112,215	—	412	5,662
Offsite Subtitle D Landfills[2]	35	79	1	56,146	—	605	3,507
Onsite and Offsite Subtitle D Landfills[1,2]	46	101	1	67,541	—	602.5	5,662
	Onsite Landfill Characteristics						
	Surface Area (acres)				1	7.13	50
	Remaining Capacity (1000 cu.yd.)				3	24.5	9,100
	Percent Remaining Capacity				0.5	5	44
	Total Capacity (1000 cu.yd.)				15	78.2	10,498
	Number of Strata in Completed Unit				0	3	400
	Depth Below Grade (ft)				0	5	15
	Height Above Grade (ft)				0	7.5	72
	# of Landfills: 16						
	Aquifer Information						
	Depth to Aquifer (ft)				12	34.5	200
	Distance to Private Well (ft)				1,000	8,970	26,800
	Population Using Private Well				1	2	3
	Distance to Public Well (ft)				5,000	10,100	58,000
	Population Using Private Well				250	1,750	2,000
	# of Aquifers: 14						
	Source:			Public	Private		
	Unreported			7	8		
	Uppermost			2	4		
	Lowermost			5	2		
	Classification of Uppermost Aquifer Current or potential source of drinking water (5) Not considered a potential source of drinking water (9)						

[1] The number of landfills characterized in Table 3.2.10 is greater than indicated in Tables 3.2.1 and 3.2.7 which focuses only on volumes generated in 1992. Table 3.2.10 incorporates data from all landfills receiving catalyst and fines in any year reported in the §3007 survey.

[2] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).

3.2.3.3 Characterization

As discussed above, the category of "catalyst and fines from catalytic cracking" as defined in the EDF consent decree includes the subcategories of "equilibrium catalyst" and "fines". These subcategories were chosen because these two residuals are generated at different points in the process and because the Agency hypothesized that the different particle sizes of catalyst and fines might result in different risk results. See Section 3.2.2 for a description of catalyst from catalytic cracking. The subcategory "fines" was further divided based on how the residual fines are collected (e.g., wet or dry scrubber systems).

Two sources of residual characterization were developed during the industry study:

- Table 3.2.11 summarizes the physical properties of the catalyst as reported in Section VII.A of the §3007 survey.

- Four catalyst fines samples were collected and analyzed by EPA. Two "dry" samples of the catalyst fines were collected from the fines storage bins at the electrostatic precipitator. Two samples of fines were collected from the wet scrubbers: one was dredged from the fines storage pond, and one was collected after the fines had been dewatered. Table 3.2.12 provides the location and description of the collected samples.

As with FCC catalyst, there is little variation in feedstocks, catalyst type, and regeneration practices across the industry and these samples are believed to be representative. Table 3.2.13 provides a summary of the characterization data collected under this sampling effort. Only constituents detected in at least one sample are shown in this table. As presented in the data, none of the FCC fines samples collected exhibited the toxicity characteristic even though heavy metals are present. High aluminum concentrations can be attributed to the silica-alumina make up of the catalyst. Because the units operate at severe operating condition, the spent catalyst fines have a very low organic content.

3.2.3.4 Source Reduction

According to the *Oil & Gas Journal*, 25% of FCC feed in the U.S. is hydroprocessed.

As discussed for FCC equilibrium catalyst, source reduction techniques are very difficult to formulate due to the limited number of inputs to the system. However, by employing process efficiency modifications and/or reuse procedures, catalyst fines can be diverted from landfilling. Examples include:

- Process modification - installing high-efficiency cyclones on the regenerator to capture a greater percentage of fines escaping with the flue gas

- Process modification - installing an ESP instead of a wet gas scrubber to enable the dry fines to be recycled

- Reuse - like equilibrium catalyst, using fines as a feedstock at cement plants.

Table 3.2.11. FCC Fines Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	53	51	3.8	6	8
Reactive CN, ppm	34	70	0	17.5	10
Reactive S, ppm	39	65	0	22.5	100
Flash Point, °C	33	71	60	89.9	125
Oil and Grease, vol%	38	66	0	0.2	1
Total Organic Carbon, vol%	31	73	0	0.12	0.35
Specific Gravity	45	59	0.78	1.5	2.32
Aqueous Liquid, %	63	41	0	13.9	75
Organic Liquid, %	60	44	0	0.07	0.01
Solid, %	95	9	56.3	90.18	100
Particle >60 mm, %	18	86	0	0	0
Particle 1-60 mm, %	20	84	0	15	100
Particle 100 μm-1 mm, %	21	83	0	21.4	100
Particle 10-100 μm, %	35	69	0	66.9	100
Particle <10 μm, %	27	77	0	34.6	100
Mean Particle diameter, microns	28	76	10	56	100

Table 3.2.12. FCC Catalyst Fines Record Sampling Locations

Sample Number	Location	Description
R2-FC-01	Shell, Wood River, IL	ESP fines
R4-FC-02	Little America, Casper, WY	ESP fines
R5-FC-02	Marathon, Garyville, LA	Wet scrubber fines
R6-FC-02	Shell, Norco, LA	Dewatered, wet scrubber fines

Table 3.2.13. FCC Fines Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Toluene	108883	1,400	< 5	< 5	< 5	354	1,400	698	925	
m,p-Xylenes	108383 / 106423	1,500	< 5	< 5	< 5	379	1,500	746	991	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Methylene chloride	75092	< 50	< 50	B 140	< 50	73	140	45	109	
Toluene	108883	< 50	B 250	< 50	< 50	100	250	100	182	
o-Xylene	95476	< 50	B 87	< 50	< 50	59	87	19	74	
m,p-Xylenes	108383 / 106423	< 50	B 210	< 50	< 50	90	210	80	156	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl)phthalate	117817	J 250	< 165	430	J 110	239	430	140	353	
2-Methylnaphthalene	91576	< 165	< 165	J 61	J 170	126	170	63	262	1, 2
1-Methylnaphthalene	90120	< 330	< 330	J 65	J 150	118	150	46	218	1, 2
Benz(a)anthracene	56553	< 165	< 165	J 76	< 165	76	76	NA	NA	1
Chrysene	218019	< 165	< 165	J 190	< 165	171	190	13	181	
Di-n-butyl phthalate	84742	< 165	< 165	J 180	< 165	169	180	8	175	
Phenanthrene	85018	< 165	< 165	570	< 165	266	570	203	432	
Pyrene	129000	< 165	< 165	J 76	< 165	76	76	NA	NA	1
Pyridine	110861	< 330	< 330	J 410	< 330	350	410	40	383	
2-Methylchrysene	3351324	< 330	< 330	J 77	< 330	77	77	NA	NA	1

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Phenol	108952	< 50	< 50	JB 13	JB 15	14	15	1	17	1, 2

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	120,000.0	73,000.0	54,000.0	17,000.0	66,000.0	120,000.0	42,856.3	101,099.3	
Antimony	7440360	47.0	< 6.0	< 6.0	< 6.0	16.3	47.0	20.5	33.0	
Arsenic	7440382	11.0	< 1.0	2.2	3.3	4.4	11.0	4.5	8.1	
Barium	7440393	160.0	590.0	55.0	210.0	253.8	590.0	233.3	444.8	
Beryllium	7440417	13.0	1.8	< 0.5	< 0.5	4.0	13.0	6.1	8.9	
Calcium	7440702	1,500.0	2,600.0	2,100.0	1,400.0	1,900.0	2,600.0	559.8	2,358.4	
Chromium	7440473	42.0	57.0	15.0	43.0	39.3	57.0	17.6	53.6	
Cobalt	7440484	26.0	18.0	< 5.0	60.0	32.8	60.0	32.9	59.7	
Copper	7440508	23.0	64.0	6.9	19.0	28.2	64.0	24.8	48.5	
Iron	7439896	6,000.0	34,000.0	1,600.0	11,000.0	13,150.0	34,000.0	14,420.7	24,960.6	
Lead	7439921	34.0	210.0	7.2	8.4	64.9	210.0	97.5	144.8	
Manganese	7439965	28.0	100.0	11.0	64.0	50.8	100.0	39.5	83.2	
Molybdenum	7439987	< 6.5	20.0	< 6.5	< 6.5	9.9	20.0	6.8	15.4	
Nickel	7440020	900.0	780.0	73.0	130.0	470.8	900.0	429.8	822.8	
Selenium	7782492	< 0.5	3.6	< 0.5	< 0.5	1.3	3.6	1.5	2.5	
Sodium	7440235	2,300.0	5,000.0	14,000.0	9,700.0	7,750.0	14,000.0	5,168.2	11,982.7	
Thallium	7440280	< 1.0	3.2	< 1.0	< 1.0	1.6	3.2	1.1	2.5	
Vanadium	7440622	2,600.0	670.0	110.0	230.0	902.5	2,600.0	1,157.0	1,850.1	
Zinc	7440666	79.0	300.0	22.0	91.0	123.0	300.0	121.8	222.7	

FCC EQUILIBRIUM CATALYST FINES

	TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								90% Confidence interval	
	CAS No.	R2-FC-01	R4-FC-02	R5-FC-02	R6-FC-02	Average Conc	Maximum Conc	Std Dev	Upper Limit	Comments
Aluminum	7429905	110.00	410.00	< 1.00	4.30	131.33	410.00	192.56	289.03	
Antimony	7440360	0.89	< 0.30	< 0.30	< 0.30	0.45	0.89	0.29	0.69	
Calcium	7440702	< 25.00	100.00	58.00	58.00	60.25	100.00	30.73	85.42	
Chromium	7440473	0.24	0.34	< 0.05	< 0.05	0.17	0.34	0.14	0.29	
Cobalt	7440484	< 0.25	< 0.25	< 0.25	0.72	0.37	0.72	0.24	0.56	
Copper	7440508	0.40	0.33	< 0.13	< 0.13	0.25	0.40	0.14	0.36	
Iron	7439896	15.00	14.00	1.60	32.00	15.65	32.00	12.49	25.88	
Manganese	7439965	0.33	2.70	0.18	0.42	0.91	2.70	1.20	1.89	
Nickel	7440020	3.40	7.50	< 0.20	0.79	2.97	7.50	3.32	5.69	
Vanadium	7440622	4.90	< 0.25	< 0.25	< 0.25	1.41	4.90	2.33	3.32	
Zinc	7440666	0.81	4.60	0.28	16.00	5.37	16.00	7.35	11.39	

Comments:
1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

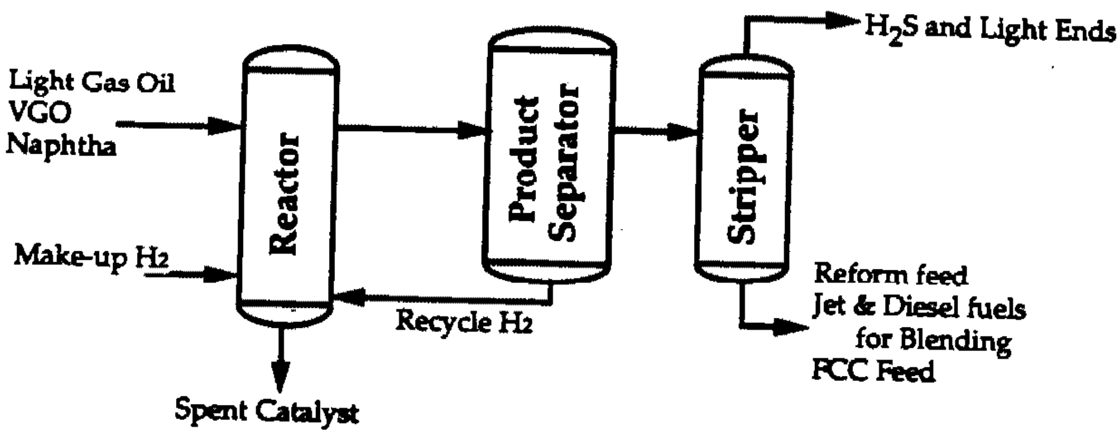
Notes:
B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.3 HYDROPROCESSING

3.3.1 Process Description

Hydroprocessing is used to remove organic sulfur or nitrogen from crude oil fractions ranging from heavy gas oils to naphthas. The hydrocarbon is heated and contacted with hydrogen. The mixture then passes to a fixed catalytic bed. In the reactor, organic sulfur and nitrogen are converted to H_2S and NH_3. In addition, metals that are present in the hydrocarbon (such as common crude elements vanadium and nickel) are adsorbed onto the catalyst, and some unsaturated compounds such as olefins or aromatics are saturated or cracked to form lighter compounds. After the reactor, fractionators or stabilizers separate the heavier hydroprocessed product from the newly formed ammonia, hydrogen sulfide, and light cracked gas. Typical reaction conditions are 550 to 850°F and 150 to 3,000 psi, with the more severe conditions used for heavier feedstocks (McKetta, 1992). A simplified process flow diagram for a typical hydroprocessing unit is shown in Figure 3.3.1.

Figure 3.3.1. Hydroprocessing Unit Process Flow Diagram



In 1993, refineries reported hydroprocessing capacity of approximately 10.6 million barrels per stream day in the United States (excluding Puerto Rico and the Virgin Islands). This compares to a total U.S. crude oil distillation capacity of approximately 15.6 million barrels per stream day. Therefore, hyproprocessing is used extensively in the refinery. The most common types of feeds are as follows (DOE's Petroleum Supply Annual 1993):

- Naphtha reformer feed (38 percent of hydroprocessing capacity). Naphthas generated from distillation, cracking, and other processes often have a low octane value. To boost octane, the stock is sent to a catalytic reforming unit. However, because sulfur is a poison to the reformer catalyst the feed is almost always hydroprocessed prior to entering the reformer reactors.

- Distillate (34 percent of hydroprocessing capacity). Distillate includes both diesel fuel and jet fuel. The 1990 Clean Air Act Amendments required the sulfur content in on-road diesel fuel to be 0.05 percent by October 1993. Many refineries have recently installed or expanded existing hydrodesulfurization reactors as a "polishing step" for their diesel fuel.

  Historically, jet fuel has required low levels of aromatics to meet specifications; these can be removed by saturation during hydroprocessing. (Another method, clay treating, also is common but is not a hydroprocessing process).

- Heavy gas oil (18 percent of hydroprocessing capacity). Heavy gas oil is a common FCC feed. Hydroprocessing reduces SO_2 emissions in the flue gas and decreases metal loadings on the FCC catalyst.

- Other/Residual (9 percent of hydroprocessing capacity). Other hydroprocessing applications include:

  - Lubricants. Paraffinic stock is processed in the lube plant by hydroprocessing to remove organic sulfur and nitrogen, saturate aromatics, and crack waxes.

  - Gas oil/residual oil. Heavy oils may be hydroprocessed as feed to a cracking unit. The extent to which these feeds are combined with heavy gas oil for DOE's calculation purposes is not known.

The above streams are associated with fuel processing operations. One other refinery hydroprocessing application, sulfur plant tail gas treating, is associated with the facility's Claus (sulfur) plant (no fuel processing is conducted at the sulfur plant). As discussed further in Section 3.9, a significant portion of sulfur unit catalyst is generated from tail gas treating. A refinery's Claus sulfur recovery unit generates an emission stream with CO_2, H_2O, and SO_2. At facilities that further remove sulfur from this emission in a tail gas treating unit, the most common approach is first to convert the SO_2 in the offgas to H_2S by hydroprocessing. Unlike other hydroprocessing units, however, there is no fractionation following the reactor because the products are all light gases. This tail gas unit catalyst is discussed here because it more closely resembles the other hydroprocessing catalysts in characterization and management than the Claus unit catalyst.

The most common hydroprocessing catalysts are nickel/molybdenum on alumina and cobalt/molybdenum on alumina. Concentrations of cobalt or nickel are approximately 2 to 3 percent, while the concentration of molybdenum is approximately 10 percent (McKetta, 1992). Hydrocracking reactors, which conduct more extensive cracking than hydroprocessing units and commonly use a different catalyst, such as nickel/tungsten, are not included in this scope of hydroprocessing. The Agency is collecting data on hydrocracking residuals separately.

3.3.2 Hydrotreating Catalyst - Residual 6

3.3.2.1 Description

The distinction between "hydrotreating" and "hydrorefining" is not a clear one. Both fall under the broad term "hydroprocessing" because both perform similar functions of desulfurization, denitrification, and saturation. EPA has chosen to distinguish the two processes by the type of feeds and the severity of treatment. Hydrotreating involves the treatment of lighter boiling stocks under less severe conditions, while hydrorefining involves the treatment of higher boiling stocks under more severe conditions. However, exceptions to these definitions result from nomenclature used by process licensors. Hydrotreating catalyst, therefore, is used in the treatment of:

- Naphtha
- Lube oils
- Some middle distillates.

Note that the *Oil & Gas Journal*'s annual report on Worldwide Refining defines hydrotreating to include "processes where essentially no reduction in the molecular size of the feed occurs." Subcategories of hydrotreating are identified as: (1) pretreating catalytic reformer feeds, (2) naphtha desulfurizing, (3) naphtha olefin or aromatics saturation, (4) straight-run distillate, (5) pretreating catalytic cracker feeds, (6) other distillates, (7) lube oil "polishing," and (8) other. The Agency believes that its definition, while simpler, is generally in keeping with the *O&GJ* definition. Further, because both hydrotreating and hydrorefining catalyst are proposed to be listed as hazardous waste, more precise definitions are not necessary.

As stated in Section 3.3.1, both carbon (from cracking reactions) and metal deposition will poison (deactivate) the hydrotreating catalyst. Catalyst life is dependent on the severity of cracking and the metals loading; changeout occurs every 1 to 5 years. The catalyst closest to the entrance (top) of the reactor becomes deactivated first, and for this reason is sometimes replaced more frequently than the whole reactor contents (this is a "topping" operation). When catalyst activity is unacceptable, the reactor is taken out of service and undergoes one or more of the following steps to reduce the hydrocarbon content of the reactor:

Catalyst Pretreatment Steps

Nitrogen sweep	87 facilities
Hydrogen sweep	80 facilities
No preparation	22 facilities
Steam stripping	5 facilities
Oxidation	10 facilities
Other/unknown	6 facilities

Source: 125 facilities reporting *in situ* treatment information from RCRA §3007 questionnaire.

- Nitrogen sweep (to remove naphtha)
- Hydrogen sweep (to burn residual hydrocarbon)
- Oxidation (to burn residual hydrocarbon)
- Steam stripping or water wash (to remove volatiles).

The vast majority of refineries uses catalyst comprised of nonprecious metal oxides on alumina. Based on a total of 349 hydrotreating reactors reporting spent catalyst generation in the questionnaire, 53 percent reported using Ni/Mo catalyst, 38 percent reported using Co/Mo catalyst, and 3 percent reported using the trimetal combination of nickel, cobalt, and molybdenum on a single catalyst or as a combination of catalysts. The remaining 6 percent reported using other metals. Precious metal hydrotreating catalyst such as palladium is reportedly used in specialized applications but was not considered by EPA to be part of the scope of the study. Hydrotreating catalyst component concentrations are presented in the following table.

Fresh Hydrotreating Catalyst Component Concentrations (wt%)

Application	NiO	CoO	MoO_3	P_2O_5	Al_2O_3
Desulfurization	--	2-5	8-20	0-2	Balance
Low severity desulfurization, denitrogenation, & olefin saturation	2-4	--	8-16	0-4	Balance
Low severity desulfurization, denitrogenation, olefin saturation, PNA saturation, mild hydrocracking	3-4	--	15-20	4-8	Balance

Source: Metal Catalyst Producers Panel of the Chemical Manufacturers Association.

Approximately 2,236 MT of the hydrotreating catalyst generated in 1992 was identified as displaying hazardous characteristics. This is approximately 40 percent of the total volume managed.

1992 Identification of Hydrotreating Catalyst from the §3007 Survey

D018 (TC benzene) 1,089 MT
D001 (Ignitable) 513 MT
D004 (TC arsenic) 440 MT

Total identified as hazardous: 2,236 MT (only the most common codes are listed; some streams carry multiple codes)

As a supplement to the listing determination effort, the Agency asked the catalyst reclaimers and regenerators to submit RCRA hazardous characteristic data, particularly the ignitable or self-heating properties, for the hydrotreating and hydrorefining catalyst they receive for regeneration or metals reclamation. Several of the reclaimers\regenerators responded to the request and a summary of their information is presented below.

CRI-MET, a metals reclaimer, typically divides the catalyst-feed into two categories: hydrotreating (HDS) and hydrorefining (resid). HDS catalyst are those which process non-residual feeds. HDS catalyst are stripped of oil prior to dumping and contain silica, arsenic, benzene, etc. CRI-MET responded that HDS catalyst have a higher potential than resid catalyst to fail the DOT self-heating test especially as they typically are dumped oil free allowing rapid access of air to any metal sulfides present in the catalyst. Resid catalyst process residual (heavy) feeds. These catalyst are rarely free of oil prior to dumping and contain elevated levels of deposited vanadium. CRI-MET has not had any resid catalyst fail DOT's test for self-heating. The large amount of oil (10-18%) which is inherently present on these catalyst effectively seals any reactive metal sulfides from oxygen. If these catalysts were oil-free, they would probably be self-heating like the HDS catalyst. CRI-MET said that approximately 25 percent of the catalyst they receive is classified as RCRA hazardous: D001 (12.55%), D001 and other (2.14%), D003 (2.24%), D003 and other (1.15%), D001 & D003 (1.19%), and other (primarily D004 & D018) (5.8%).

CRI International, Inc. (CRII), a catalyst regenerator, provided hazardous characteristic information for the hydrotreating, hydrorefining and various petrochemical catalyst they receive for regeneration. Table 3.3.1 provides the customer classification data of the spent catalyst shipped to CRII's Lafayette, Louisiana regeneration facility. CRII also stated that due to the pyrophoric/self-heating tendency of the catalyst they experience 3 to 5 uncontrolled temperature exotherms each year in their dust collector and 5 to 7 times per year the plants have experienced uncontrolled exotherms of the spent catalyst. CRII stated that due to the "absence of a really definitive test" for self-heating characteristics these spent catalyst may or may not have been identified as potential self-heating or pyrophoric material.

Table 3.3.1. CRII Ignitability and Reactivity Data for Hydroprocessing Catalysts

Hazardous Characteristic	1992 (tons)	1993 (tons)	1994 (tons)
D001	1,035.4	2,017.7	533.7
D003	0	46.8	337.7
D001, D003	0	166.5	99.3
D001, D018	378.5	74.4	580.2
D003, D018	224.8	0	0
D001, D003, D018	50.7	228.8	327.4
Total Ignitability & Reactivity	1,689.4	2,534.3	1,878.3
Total Regeneration	3,000	2,900	3,900

Gulf Chemical & Metallurgical Corporation (GCMC), a catalyst metals reclaimer, also provided pyrophoric/self-heating and ignitability information for the hydrotreating and hydrorefining catalysts. GCMC conducted a study to determine the effect of hydrocarbon content on the catalyst's flash point and the effect of the free oil content on the self-heating characteristic. The following summarizes their results.

- The catalyst flash point was reduced by adding free oil. The addition of 16% free oil reduced the flash point from 280° to 195°F. The presence of light hydrocarbons, with flash points below 140°F, could change the ignitability of spent catalyst. The study of the effect of different types of oil on the flash point was not part of this work.

- RCRA non-hazardous spent catalyst clearly exhibited self-heating characteristics when held in an oven at 140°C for 24 hours. The chemical changes increased the temperature of the sample to 257°C.

- The volume of material and the availability of oxygen affect self-heating characteristics. The temperature at the beginning of the test was between 80° and 175°C depending on depth. The heat generated in a pile of catalyst stored outdoors increased the temperature of the pile, 3 feet below the surface, to 320°C in 30 days. At 6 feet below surface, the final temperature was 235°C and 140°C at 10 feet. The temperature increase was almost linear at a rate of 7°C per day.

- Spent catalyst stored in piles exhibit self-heating and self-ignition characteristics.

3.3.2.2 Generation and Management

The spent catalyst is vacuumed or gravity dumped from the reactors. Based on information from site visits, most refineries place the material directly into closed containers such as 55-gallon drums or flow-bins. The RCRA §3007 questionnaire and site visits indicate that very few of refineries use other interim storage methods.

Ninety-two facilities reported generating a total quantity of 5,640 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "spent hydrotreating catalyst" if they were assigned a residual identification code of "spent solid catalyst" or "solid catalyst fines" and were generated from a process identified as a hydrotreating unit. These correspond to residual codes 03-A and 03-B, respectively, in Section VII.2 of the questionnaire and process code 06 in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all hydrotreating catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2. Based on the results of the questionnaire, 131 facilities use hydrotreating units and thus are likely to generate spent hydrotreating catalyst. Due to the infrequent generation of this residual, not all of these 131 facilities generated spent catalyst in 1992. However, 1992 is expected to be a typical year in regard to catalyst change-out volume and management.

Table 3.3.2 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.3.2. Generation Statistics for Spent Hydrotreating Catalyst, 1992

Final Management	# of Streams	# of Streams w/ unreported volume	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Transfer metal catalyst for reclamation or regeneration	122	8	4,274	35	100 (estimate)
Disposal offsite in Subtitle C landfill	21	2	639	30	71
Disposal in offsite Subtitle D landfill	20	1	408	20	56
Reuse[1]	8	0	202	25	85
Other offsite management[2]	3	0	43	14.4	26
Disposal in onsite Subtitle D landfill	3	0	12	4	12
Onsite land treatment	1	0	7	7	7
Storage/unknown offsite[3]	5	0	56	11	35.2
TOTAL	184	17	5,640	31	77.4

[1] Onsite reuse includes reuse as catalyst in the same or a similar unit, and reuse of catalyst support balls.
[2] Other offsite management includes incineration and stabilization.
[3] Storage/unknown offsite includes (1) onsite storage with no final management and (2) transfer to an unspecified offsite facility.

Plausible management scenarios were chosen by EPA on which to perform risk assessment modeling. The scenarios were chosen based on the existing and possible "high potential exposure" disposal practices currently used. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.3.2 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite Subtitle D landfilling (used for 0.2 percent of the total residual volume). An onsite monofill scenario was rejected because of the intermittent (less than once per year) generation frequency which is not typical of waste that tends to be monofilled.

- Offsite Subtitle D landfilling (used for 7 percent of the total residual volume).

The risk assessment input quantities for modeling releases using these scenarios were derived from the distribution of volumes from all management practices except for Subtitle C landfilling. These input values were greater than those associated with Subtitle D landfilling. The Agency chose this approach to determining risk assessment model input parameters after evaluating current trends in management practices. Information provided by catalyst reclaimers such as CRI-MET indicates that refineries have been shifting from reclamation to landfilling because of the depressed metals markets. This economic factor has made landfilling significantly more cost-effective than reclamation (aside from any potential liability reductions associated with reclamation). EPA predicted that if the risk assessment modeling were to show no basis for listing hydroprocessing catalysts, the trend to increase landfilling would be accelerated. As a result, the Agency determined that it was appropriate to consider the entire distribution of volumes reported in 1992 in creating the risk assessment inputs, rather than limiting the inputs to those catalysts reported to be landfilled in Subtitle D units. The only exception was those volumes reported to be managed in Subtitle C units which were assumed to be characteristic and thus would never be managed in Subtitle D units.

The dominant management method for this residual, transfer for offsite metals reclamation/regeneration, was not selected for modeling risks. A small number of catalyst reclaimers service the refining industry, such as CRI-MET in Louisiana and Gulf Metallurgical in Texas, and reclaim spent catalyst for its vanadium, nickel, and molybdenum metal values. EPA conducted engineering site visits to both facilities. Both of these reclamation facilities routinely manage both characteristically hazardous and nonhazardous spent catalysts. One facility segregates the hazardous and nonhazardous feedstocks but following storage, both the hazardous and nonhazardous feeds are subjected to the same process. Therefore, risks from processing are equal for both characteristic and nonhazardous wastes.

A more detailed study of the catalyst recycling industry would be a significant endeavor, and was determined to be outside the scope of this listing determination. Based on the site visits described above, EPA believes that the practice of spent catalyst reclamation is valuable because it is consistent with the intent of RCRA and because, based on EPA's preliminary review of this industry, the spent catalysts appear to be managed and processed in a way that controls risks.

Two volume scenarios were used in the risk assessment:

- Using volume statistics for all management practices except those in a Subtitle C landfill. This assumption reflects the theory that a "no-list" decision might encourage refineries to choose Subtitle D landfilling over metals reclamation (which is a cost-effective choice only when metals prices or liability concerns are high).

- Use statistics for all wastes landfilled in Subtitle D landfills. This assumption is consistent with all other landfilled wastes.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.3.3. The Agency evaluated whether to model interim storage practices, in addition to the final management practices described in Table 3.3.3. Based on the engineering site visits and sampling trips, the Agency believes that on-site storage of these residuals is infrequent (i.e., the catalysts are only generated every 2-5 years), short term in nature due to space constraints on the unit and costs associated with container rental, and carefully controlled due to the potential pyrophoric nature of the residual (e.g., in closed flobins under an inert gas blanket).

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.3.4 provides a summary of the data for the targeted management practices used in the risk assessments for this residual. This table is developed using the RCRA §3007 survey of facilities reporting onsite landfilling of hydrotreating catalyst in any reported year. The survey specified, that if the residual was not generated in 1992, to provide the information for the last year the residual was generated.

Table 3.3.3. Selection of Risk Assessment Modeling Scenario: Spent Hydrotreating Catalyst

Final Management	Basis for Consideration in Risk Assessment
Transfer metal catalyst for reclamation or regeneration	Not modeled, see discussion on previous page
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal in offsite Subtitle D landfill	Modeled
Onsite reuse[1]	Not modeled, excluded management practice
Other offsite management[2]	Not modeled, minor volumes
Disposal in onsite Subtitle D landfill	Modeled
Onsite land treatment	Not modeled, *de minimis* volume (< 10 MT) unlikely to present risk
Storage/unknown offsite[3]	Not modeled, minimal volume; no defined release path of concern

[1] Onsite reuse includes reuse as catalyst in the same or a similar unit, and reuse of catalyst support balls.
[2] Other offsite management includes incineration and stabilization.
[3] Storage/unknown offsite includes (1) onsite storage with no final management and (2) transfer to an unspecified offsite facility. Interim storage was not modeled between release pathway would be unlikely due to widespread use of closed containers.

Table 3.3.4. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RCs**	**# RC w/ unreported volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**Mean Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfills[2,3]	13	23	1	419	—	20	70
All Management Practices Except Subtitle C Landfills[1,3]	—	163	15	5,000	—	20	77.4
	Onsite Landfill Characteristics						
	Surface Area (acres)				0.02	7.38	30
	Remaining Capacity (cu.yd.)				280	30,735	838,000
	Percent Remaining Capacity				2	9	80
	Total Capacity (cu.yd.)				400	83,900	840,000
	Number of Strata in Completed Unit				0	8	16
	Depth Below Grade (ft)				3	18	50
	Height Above Grade (ft)				0	0	12
	# of Landfills: 5						
	Aquifer Information						
	Depth to Aquifer (ft)				14	39	265
	Distance to Private Well (ft)				3,500	8,970	26,400
	Population Using Private Well				1	1	1
	Distance to Public Well (ft)				13,200	26,400	58,000
	Population Using Public Well				1,500	1,500	1,500
	# of Aquifers: 5						
	Source:		Public	Private			
	Unreported		3	1			
	Uppermost		1	2			
	Lowermost		1	1			
	Combination		0	1			
	Classification of Uppermost Aquifer: Current or potential source of drinking water (1) Not considered a potential source of drinking water (4)						

[1] The number of onsite landfills characterized in this table is greater than indicated in Table 3.3.2, which focuses only on volumes generated in 1992. Table 3.3.4 incorporates data from all onsite landfills receiving catalyst in any year reported in the §3007 survey.
[2] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).
[3] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.3.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.3.5 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- Six record samples of spent hydrotreating catalyst were collected and analyzed by EPA. These spent catalysts represent the various types of applications and active metals used by the industry and are summarized in Table 3.3.6.

The collected samples are expected to be representative of naphtha hydrotreaters and other distillate hydrotreaters. These comprise the majority of hydrotreating applications. Five of the six samples represent naphtha feeds. This is well represented for one of the principal services of hydrotreating reactors, but does not represent other applications such as jet fuel hydrotreating. However, contaminants potentially present in naphtha feeds would likely be present in other distillate hydrocarbon feeds. Therefore, spent catalyst from these applications should be similar to spent catalyst from other feeds because the same function of desulfurization is being performed. Five of the six samples represent nickel/molybdenum catalyst. As discussed earlier, almost all reactors use Ni/Mo and/or cobalt/molybdenum, with slightly more using nickel/molybdenum. This split, therefore, is representative of most hydrotreating functions. Additionally, the samples represent different catalyst pretreatment techniques. One of the samples was taken from catalyst that did not undergo a carbon burn prior to dumping. However, it is expected to be representative because, based on the results of the RCRA §3007 questionnaire, not all catalysts undergo carbon burn.

Other hydrotreating applications account for a small percentage of the hydrotreating universe. Hydrotreating applications for lubricants include lube oil hydrotreating, wax hydrotreating, and catalytic dewaxing (used to crack waxes in lube oils) and are used by 20 facilities. According to the RCRA §3007 questionnaires, most (75 percent) of these facilities use Ni/Mo catalyst. Other catalysts such as Co/Mo, Ni/W, and palladium are used less frequently. Hydrotreating units with palladium catalyst are specifically excluded from the scope of this study because only non-precious metal catalysts were the subject of the EPA/EDF consent decree with respect to hydrotreating (based on a review of the underlying documents used in development of the consent decree language (i.e., refer to MRI report)).

Spent Catalyst Composition	
Al_2O_3	35-45%
Oil	0-18%
C	4-16%
V	0-10%
Ni	0-3%
Co	0-3%
Mo	6-10%
S	6-12%
Fe	0-2%
As	0-0.5%
H_2O	varies
F, Cl, P, B, Si, etc., varies	

All six samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. Three of the samples were found to exhibit the toxicity characteristic for benzene (i.e., the level of benzene in these samples' TCLP extracts exceeded the corresponding regulatory level). The high aluminum, molybdenum, nickel, and cobalt concentrations can be attributed to the catalyst make up: nickel/molybdenum or cobalt/molybdenum on alumina. A summary of the results is presented in Table 3.3.7. Only constituents detected in at least one sample are shown in this table.

Due to the pyrophoric nature of the spent catalyst, at least 2 refineries would not allow sample collection from the flow-bins once they had been sealed. One refinery requested the sample be stored in an inert atmosphere to decrease the possibility of the sample igniting. Another refinery would not allow sample collection due to a possible presence of nickel carbonyl.

Table 3.3.5. Hydrotreating Catalyst Physical Properties

Properties	# of Values	# of Unreported Values	10th %	Mean	90th %
pH	132	259	4.2	6.4	8.2
Reactive CN, ppm	102	289	0.03	30.7	50
Reactive S, ppm	122	269	1.0	845	160
Flash Point, C	112	279	43.3	84	127
Oil and Grease, vol%	59	328	0	3.6	9.0
Total Organic Carbon, vol%	52	339	0	4.0	10
Specific Gravity	94	297	0.66	1.10	2.06
BTU Content, BTU/lb	27	364	0	1,244	6,177
Aqueous Liquid, %	179	212	0	1.3	2.0
Organic Liquid, %	180	211	0	0.5	1.0
Solid, %	289	102	96.5	98.8	100
Particle >60 mm, %	86	305	0	21	100
Particle 1-60 mm, %	117	274	0	83	100
Particle 100 μm-1 mm, %	81	310	0	7.8	10
Particle 10-100 μm, %	66	325	0	2.1	1.0
Particle <10 μm, %	65	326	0	0.3	0
Mean Particle diameter, microns	37	349	0	2100	3,200

Table 3.3.6. Hydrotreating Catalyst Record Sampling Locations		
Sample number	**Facility**	**Description: Type of Feed, Catalyst**
R1-TC-01	Marathon, Indianapolis, IN	Naphtha reformer feed, Co/Mo catalyst
R8A-TC-01	Amoco, Texas City, TX	FCC feed, Ni/Mo catalyst
R3B-TC-01	Exxon, Billings, MT	Naphtha, Ni/Mo catalyst
R11-TC-01	ARCO, Ferndale, WA	Naphtha, Ni/Mo catalyst
R22-TC-01	Star, Port Arthur, TX	FCC feed[1], Ni/Mo catalyst
R18-TC-01	Ashland, Canton, OH	Naphtha reformer/isomerization feed, Ni/Mo catalyst

[1] A unit accepting FCC feed would typically be designated as hydrorefining; however, the generating facility designated this sample to be hydrotreating catalyst.

3.3.2.4 Source Reduction

Little can be done to reduce the quantity of these generated catalysts since, by design, they must be periodically replaced with fresh catalyst. The greatest waste minimization opportunities arise from sending these materials offsite for metals regeneration, reclamation or other reuse.

The engineering site visits reported some incremental process or treatment modifications that can result in lower volumes of spent catalyst or lower risk/toxicity. These include:

- Offsite regeneration and reintroduction to reactor results in lower volumes of catalyst being disposed or reclaimed.
- Separation of support material for onsite reuse reduces the volume of material sent offsite.
- Upstream process changes to eliminate catalyst poisons reduce the frequency of catalyst turnover.

In addition, the literature reports some operational modifications that can be used to decrease spent catalyst generation. These are summarized in Table 3.3.8.

Table 3.3.7. Residual Characterization Data for Spent Hydrotreating Catalyst

Volatile Organics – Method 8260A µg/kg

	CAS No.		R1-TC-01		R8A-TC-01		R11-TC-01		R3B-TC-01		R18-TC-01		R22-TC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432		500,000	J	9,400		24,000		2,000		160,000		2,900	116,383	500,000	197,467	235,364	
n-Butylbenzene	104518	<	12,500		50,000	<	625		3,700	<	600		2,000	11,571	50,000	19,346	23,228	
sec-Butylbenzene	135988	<	12,500		17,000	<	625	J	1,100	<	600		3,800	5,936	17,000	7,073	10,189	
tert-Butylbenzene	98066	<	12,500	<	6,250	<	625	<	625	J	410	<	625	410	410	NA	NA	1
Ethylbenzene	100414		280,000		110,000		13,000		5,900	J	1,100		22,000	72,000	280,000	109,622	138,055	
Isopropylbenzene	98828		26,000		32,000	J	600		1,300	<	600		6,000	11,450	32,000	14,001	19,868	
p-Isopropyltoluene	99876	<	12,500		25,000	<	625	J	1,250	<	600		1,600	6,963	25,000	9,959	12,964	
n-Propylbenzene	103651		62,000		57,000		1,300		3,600	J	440		10,000	22,390	62,000	28,963	39,654	
Methyl ethyl ketone	78933	<	12,500	<	6,250	<	625	<	625		9,500	<	625	3,525	9,500	4,134	6,359	1
Toluene	108883		1,300,000		120,000	<	625		16,000		7,900		30,000	245,754	1,300,000	518,314	558,077	
1,2,4-Trimethylbenzene	95636		310,000		220,000		2,500		22,000		9,700		15,000	96,533	310,000	133,714	177,108	
1,3,5-Trimethylbenzene	108678		120,000		62,000	J	1,060		6,500		2,500		10,000	33,677	120,000	48,143	62,667	
o-Xylene	95476		370,000		140,000		11,000		13,000		3,500		45,000	97,083	370,000	143,022	183,265	
m,p-Xylenes	108383 / 106423		550,000		280,000		34,000		30,000		12,000		99,000	167,500	550,000	211,926	295,201	
Naphthalene	91203	<	12,500		180,000	<	625		6,700	J	140	<	625	33,432	180,000	71,966	76,797	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R1-TC-01		R8A-TC-01		R11-TC-01		R3B-TC-01		R18-TC-01		R22-TC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Methylene chloride	75092	<	50		610		950		410	<	50	<	50	353	950	374	579	
Benzene	71432		39,000		170		3,700	J	48		4,200		250	7,895	39,000	15,352	17,149	
Ethylbenzene	100414		3,000		220	J	64	J	24	<	50		880	705	3,000	1,170	1,410	
Methyl ethyl ketone	78933	<	50	<	50	<	50	<	50		520	<	50	128	520	192	244	
Toluene	108883		39,000		740		1,600		210		100		4,200	7,675	39,000	15,421	16,967	
1,2,4-Trimethylbenzene	95636	<	50		160	<	50	<	50	<	50		120	83	160	55	118	
1,3,5-Trimethylbenzene	108678	<	50	<	50	<	50	<	50	<	50		300	92	300	102	153	
o-Xylene	95476		4,700		340	J	48	J	59	<	50		840	1,006	4,700	1,836	2,112	
m,p-Xylene	108383 / 106423		13,000		520		150		130	J	46		3,000	2,808	13,000	5,119	5,892	
Naphthalene	91203	<	50		200	<	50	<	50	<	50	<	50	75	200	61	112	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R1-TC-01		R8A-TC-01		R11-TC-01		R3B-TC-01		R18-TC-01		R22-TC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl) phthalate	117817	<	660	<	4,125	<	165	<	165	J	120		580	258	580	216	434	1
Di-n-butylphthalate	84742	<	660	<	4,125	<	165	<	165	J	110	<	165	110	110	NA	NA	1
Benz(a)anthracene	56553	<	660	J	14,000	<	165	<	165	<	165	<	165	2,553	14,000	5,611	5,934	
Benzo(a)pyrene	50328	<	660	J	14,000	<	165	<	165	<	165	<	165	2,553	14,000	5,611	5,934	
Carbazole	86748	<	1,320		120,000	<	330	<	330	<	330	J	92	20,400	120,000	48,796	49,803	
Chrysene	218019	<	660		24,000	<	165	<	165	<	165	<	165	4,220	24,000	9,692	10,050	
Dibenzofuran	132649	<	660		36,000	<	165	<	165	<	165	J	72	6,538	36,000	15,415	15,826	
Fluoranthene	206440	<	660		34,000	<	165	<	165	<	165	<	165	5,887	34,000	13,774	14,187	
Fluorene	86737	<	660		130,000	<	165	<	165	<	165		420	21,929	130,000	52,944	53,803	
2,4-Dimethylphenol	105679	J	270	<	4,125		830	<	165	J	310		750	465	830	303	673	1
2-Methylphenol	95487		6,800	<	4,125		2,600	<	165		1,200	<	165	2,543	6,800	2,600	4,109	
3/4-Methylphenol	NA		4,200	<	4,125		2,100	<	165		950	<	165	1,951	4,200	1,854	3,068	
Phenol	108952		8,200	<	4,125		1,800	<	165		3,400	<	165	2,976	8,200	3,032	4,800	
Phenanthrene	85018	<	660		400,000	<	165	<	165	<	165	J	300	66,909	400,000	163,161	165,238	
Pyrene	129000	<	660		530,000	<	165	<	165	<	165	J	310	88,578	530,000	216,252	218,885	
1-Methylnaphthalene	90120	J	260		630,000	<	330	J	640	<	330	<	330	105,315	630,000	257,042	260,202	
2-Methylnaphthalene	91576	J	460		1,000,000	<	165		1,200	J	230		480	167,089	1,000,000	408,041	412,965	
2-Methylchrysene	3351324	<	1,320	J	58,000	<	330	<	330	<	330	<	330	10,107	58,000	23,468	24,247	
Naphthalene	91203	J	1,000		250,000	<	165		1,100		400	J	140	42,134	250,000	101,834	103,497	

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/kg

	CAS No.	R1–TC–01	R8A–TC–01	R11–TC–01	R38–TC–01	R18–TC–01	R22–TC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	< 50	J 12	< 50	< 50	< 50	< 50	12	12	NA	NA	1
Bis(2–ethylhexyl) phthalate	117817	270	130	JB 22	< 50	< 50	< 50	95	270	93	151	
Carbazole	86748	< 100	J 59	< 100	< 100	< 100	< 100	59	59	NA	NA	1
Di–n–butyl phthalate	84742	< 50	< 50	J 13	< 50	< 50	< 50	13	13	NA	NA	1
2,4–Dimethylphenol	105679	J 28	J 48	110	J 13	< 50	J 53	50	110	33	70	
2–Methylphenol	95487	J 80	J 99	430	< 50	J 16	J 99	129	430	151	220	
3/4–Methylphenol (total)	NA	< 50	J 75	790	< 50	J 12	J 96	179	790	301	380	
Phenol	108952	J 28	< 50	1,000.00	< 50	170	J 63	227	1,000	382	457	
Fluorene	86737	< 50	J 14	< 50	< 50	< 50	< 50	14	14	NA	NA	1
1–Methylnaphthalene	90120	< 100	J 180	< 100	< 100	< 100	< 100	113	180	33	133	
2–Methylnaphthalene	91576	< 50	230	< 50	< 50	< 50	< 50	80	230	73	124	
Naphthalene	91203	< 50	170	< 50	< 50	< 50	< 50	70	170	49	100	
Phenanthrene	85018	< 50	J 16	< 50	< 50	< 50	< 50	16	16	NA	NA	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R1–TC–01	R8A–TC–01	R11–TC–01	R38–TC–01	R18–TC–01	R22–TC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	370,000	150,000	190,000	220,000	330,000	200,000	243,333	370,000	86,641	295,541	
Antimony	7440360	< 30.0	< 60.0	< 6.0	< 6.0	< 30.0	17.0	9.7	17.0	6.4	16.6	1
Arsenic	7440382	120.0	71.0	42.0	1,600.0	66.0	460.0	393.2	1,600.0	611.5	761.8	
Beryllium	7440417	< 2.5	5.7	1.9	< 1.0	< 2.5	1.6	2.5	5.7	1.7	3.5	
Cadmium	7440439	12.0	< 0.5	< 0.5	< 1.0	< 2.5	1.7	3.0	12.0	4.5	5.7	
Calcium	7440702	< 2,500.0	5,700.0	< 500.0	< 1,000.0	< 2,500.0	< 500.0	2,116.7	5,700.0	1,980.3	3,310.0	
Chromium	7440473	63.0	19.0	2.4	18.0	< 5.0	16.0	20.6	63.0	21.9	33.8	
Cobalt	7440484	28,000.0	34.0	78.0	67.0	< 25.0	4,400.0	5,434.0	28,000.0	11,191.1	12,177.5	
Copper	7440508	52.0	22.0	43.0	33.0	< 12.5	14.0	29.4	52.0	16.0	39.1	
Iron	7439896	6,000.0	1,200.0	470.0	4,000.0	1,100.0	1,800.0	2,428.3	6,000.0	2,132.1	3,713.1	
Lead	7439921	3.5	7.2	0.8	4.0	35.0	130.0	30.1	130.0	50.6	60.5	
Manganese	7439965	< 7.5	3.8	< 1.5	< 3.0	< 7.5	120.0	23.9	120.0	47.2	52.3	
Molybdenum	7439987	87,000.0	17,000.0	69,000.0	77,000.0	[redacted]	48,000.0	[redacted]	87,000.0	27,099.8	80,329.7	3
Nickel	7440020	66.0	25,000.0	20,000.0	20,000.0	[redacted]	7,500.0	[redacted]	25,000.0	10,030.8	22,136.7	3
Selenium	7782492	63.0	< 2.5	33.0	210.0	100.0	< 2.5	68.5	210.0	78.6	116.0	
Sodium	7440235	< 2,500.0	< 500.0	< 500.0	3,800.0	< 2,500.0	10,000.0	3,300.0	10,000.0	3,524.2	5,423.6	
Thallium	7440280	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	2.8	1.3	2.8	0.7	1.7	
Vanadium	7440622	390.0	3,300.0	150.0	< 10.0	160.0	1,800.0	968.3	3,300.0	1,319.4	1,763.4	
Zinc	7440666	< 10.0	140.0	< 2.0	25.0	54.0	54.0	47.5	140.0	50.2	77.8	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R1–TC–01	R8A–TC–01	R11–TC–01	R38–TC–01	R18–TC–01	R22–TC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	93.00	2.80	< 1.00	< 1.00	5.20	< 1.00	17.33	93.00	37.11	39.69	
Arsenic	7440382	< 0.05	4.90	< 0.05	< 0.05	< 0.03	1.50	1.10	4.90	1.95	2.27	
Cadmium	7440439	0.06	< 0.03	< 0.03	< 0.03	< 0.01	< 0.03	0.03	0.06	0.02	0.05	
Calcium	7440702	< 25.00	200.00	< 25.00	< 25.00	< 12.50	< 25.00	52.08	200.00	72.64	95.65	
Cobalt	7440484	310.00	< 0.25	< 0.25	< 0.25	< 0.13	20.00	55.15	310.00	125.10	130.53	
Iron	7439896	3.40	1.20	9.20	< 0.50	7.50	60.00	13.63	60.00	22.97	27.48	
Manganese	7439965	0.22	1.40	0.16	< 0.08	0.30	4.00	1.03	4.00	1.54	1.95	
Molybdenum	7439987	21.00	2.80	11.00	12.00	11.00	48.00	17.63	48.00	15.96	27.25	
Nickel	7440020	0.91	37.00	250.00	210.00	310.00	67.00	145.82	310.00	127.26	222.50	
Vanadium	7440622	< 0.25	6.60	< 0.25	< 0.25	< 0.13	< 0.25	1.29	6.60	2.60	2.86	
Zinc	7440666	< 0.10	1.70	1.00	< 0.10	0.25	0.44	0.60	1.70	0.64	0.98	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.
3 CBI redacted information falls within the range of concentrations of other samples.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

Table 3.3.8. Documented Source Reduction Options for Hydrotreating Catalyst	
Reference	Waste Minimization Methods
McKetta, 1992	Guard columns can be used to adsorb metals that would otherwise deactivate the main column.
Monticello, D.J. "Biocatalytic Desulfurization." *Hydrocarbon Processing*. February 1994.	Material substitution (eliminating use of metallic catalysts).
"NPRA Q&A 1: Refiners Focus on FCC, Hydroprocessing, and Alkylation Catalyst." *Oil & Gas Journal*. March 28, 1994.	Regeneration. Top-bed skimming.
Gorra, F., Scribano, G., Christensen, P., Anderson, K.V., and Corsaro, O.G. "New Catalyst, Improve Presulfiding Result in 4+ Year Hydrotreater Run." *Oil & Gas Journal*. August 23, 1993.	Material substitution.
"Petroleum-derived Additive Reduces Coke on Hydrotreating Catalyst." *Oil & Gas Journal*. December 27, 1993.	Process modification.
Berrebi, G., Dufresne, P., and Jacquier, Y. "Recycling of Spent Hydroprocessing Catalysts: EURECAT Technology." *Environmental Progress*. May 1993.	Metals reclamation.

3.3.3 Hydrorefining Catalyst - Residual 7

3.3.3.1 Description

Hydrorefining catalyst is generated in a manner similar to hydrotreating catalyst. Units generating hydrorefining catalyst include the following:

- Gas oil desulfurization
- Residual desulfurization
- Desulfurization of some middle distillates.

Note that the *Oil & Gas Journal*'s annual report on Worldwide Refining defines hydrorefining to include "process where 10% of the feed or less is reduced in the molecular size." Subcategories of hydrorefining are identified as: (1) residual desulfurization, (2) heavy gas oil desulfurization, (3) catalytic cracker and cycle stock, (4) middle distillate, and (5) other. The Agency believes that its definition, while simpler, is generally in keeping with the *O&GJ* definition.

The poisoning mechanisms for hydrorefining catalyst are similar to those for hydrotreating catalyst and catalyst removal is conducted in the same way. However, some facilities take great care to keep the hydrorefining catalyst in an inert atmosphere during all phases of catalyst removal. This is because ferric sulfide, a byproduct of the reaction, can react with oxygen and cause pyrophoricity.

When catalyst activity is unacceptable (every 1 to 5 years), the reactor is taken out of service and undergoes one or more of the following steps to reduce the hydrocarbon content of the reactor:

- Nitrogen sweep (to remove naphtha)
- Hydrogen sweep (to burn residual hydrocarbon).

Catalyst Pretreatment Steps

Nitrogen sweep	41 facilities
Hydrogen sweep	37 facilities
No preparation	5 facilities
Neutralization/ other/unknown	11 facilities

Source: 53 facilities reporting *in situ* treatment information from RCRA §3007 questionnaire.

The vast majority of refineries uses catalyst comprised of nonprecious metal oxides on alumina. Based on a total of 114 hydrorefining reactors reporting spent catalyst generation in the questionnaire, 50 percent reported using Ni/Mo catalyst, 35 percent reported using Co/Mo catalyst, and 11 percent reported using the combination of nickel, cobalt, and molybdenum (either as one catalyst or as a mixture of catalysts). The remaining 4 percent report using miscellaneous combinations of these metals. Usage of precious metal hydrorefining catalyst, if any, was not investigated by EPA as part of the scope of the study. Hydrorefining catalyst component concentrations are presented in the following table.

Approximately 5,028 MT of hydrorefining catalyst generated in 1992 were identified as displaying hazardous characteristics. This is approximately 27 percent of the total volume managed. For more information on hazardous characteristics and the pyrophoric or self-heating tendencies of hydrotreating and hydrorefining catalysts refer to Section 3.3.2.1.

1992 Identification of Hydrorefining Catalyst

D018 (TC benzene) 3,164 MT
D001 (Ignitable) 1,671 MT
D004 (TC arsenic) 755 MT

Total identified as hazardous: 5,028 MT (only the most common codes are listed; some streams carry multiple codes)

Fresh Hydrorefining Catalyst Component Concentrations (wt%)					
Application	**NiO**	**CoO**	**MoO_3**	**P_2O_5**	**Al_2O_3**
Fixed bed, NiMo	2-5	--	12-18	0-7	Balance
Fixed bed, CoMo	--	2-5	12-18	0-5	Balance
Ebullating bed	3-4	--	12-18	0-2	Balance

Source: Metal Catalyst Producers Panel of the Chemical Manufacturers Association.

3.3.3.2 Generation and Management

The spent catalyst is vacuumed or gravity dumped from the reactors. Based on information from site visits, most refineries place the material directly into closed containers such as 55-gallon drums or flow-bins. The RCRA §3007 questionnaire and site visits indicate that few refineries use other interim storage methods.

Thirty-eight facilities reported generating a total quantity of 18,634 MT of this residual in 1992, according to the 1992 RCRA §3007 questionnaire. Residuals were assigned to be "spent hydrorefining catalyst" if they were assigned a residual identification code of "spent solid catalyst" or "solid catalyst fines" and were generated from a process identified as a hydrorefining unit. These correspond to residual codes 03-A and 03-B, respectively, in Section VII.2 of the questionnaire and process code 07 in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all hydrorefining catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2. Based on the results of the questionnaire, 58 facilities use hydrorefining units and thus likely generate spent hydrorefining catalyst. Due to the infrequent generation of this residual, not all of these 58 facilities generated spent catalyst in 1992. However, 1992 is expected to be a typical year in regard to catalyst change-out volume and management.

Table 3.3.9 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.3.9. Generation Statistics for Spent Hydrorefining Catalyst, 1992

Final Management	# of Streams	# of Streams with unreported volume	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Transfer metal catalyst for reclamation or regeneration	63	0	15,359	244	500 (estimate)
Disposal offsite in Subtitle D landfill	5	0	2,348	470	2,099[1]
Disposal onsite in Subtitle D landfill	1	0	700	700	700
Disposal offsite in Subtitle C landfill	2	0	198	99	151
Offsite recycle	1	0	29	29	29
TOTAL	72	0	18,634	255	500

[1] This particularly high volume was verified with the generating facility; the spent catalyst was generated from a large unit.

Plausible management scenarios were chosen by EPA on which to perform risk assessment modeling. The scenarios were chosen based on the existing and possible "high potential exposure" disposal practices currently used. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.3.9 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment.

The selected management practices are:

- Onsite Subtitle D landfilling (used for 4 percent of the total residual volume). An onsite monofill scenario was rejected because of the intermittent (less than once per year) generation frequency which is not typical of waste that tends to be monofilled.

- Offsite Subtitle D landfilling (used for 13 percent of the total residual volume)

The input quantities for modeling releases using these scenarios were greater than those actually landfilled in 1992. Instead, the management quantity is assumed to be the total quantity generated (minus that managed in Subtitle C units already). This is because other management methods, in particular reclamation, could change to landfilling in the future due to economic factors, convenience, or other factors. See Section 3.3.2.2 for additional details.

As with the hydrotreating catalyst, the Agency determined that it was unnecessary to model interim storage prior to final management.

The management method accounting for the majority of the residual, transfer for offsite metals reclamation/regeneration, was not selected for modeling risks. A small number of catalyst reclaimers, such as CRI-MET in Louisiana and Gulf Metallurgical in Texas, reclaim spent catalyst for its vanadium, nickel, and molybdenum metal values. Both of these reclamation facilities routinely manage both characteristically hazardous and nonhazardous spent catalysts. One of these facilities segregates the hazardous and nonhazardous feedstocks, but following storage, both the hazardous and nonhazardous feeds are subjected to the same process. Therefore, risks from processing are equal for both characteristic and nonhazardous wastes.

A more detailed study of the catalyst recycling industry would be a significant endeavor, and was determined to be outside the scope of this listing determination. Based on the site visits described above, EPA believes that the practice of spent catalyst reclamation is valuable because it is consistent with the intent of RCRA and because, based on EPA's preliminary review of this industry, the spent catalysts appear to be managed and processed in a way that controls risks.

Two volume scenarios were used in the risk assessment:

- Using volume statistics for all management practices except those in a Subtitle C landfill. This assumption reflects the theory that a "no-list" decision would encourage refineries to choose Subtitle D landfilling over metals reclamation (which is a cost-effective choice only when metals prices or liability concerns are high).

- Use statistics for all wastes landfilled in Subtitle D landfills. This assumption is consistent with all other landfilled wastes.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.3.10.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.3.11 provides a summary of the data for the targeted management practices used in the risk assessment for this residual. This table is developed from facilities reporting onsite landfilling of hydrorefining catalyst in any year according to the RCRA §3007 survey.

Table 3.3.10. Selection of Risk Assessment Modeling Scenario: Spent Hydrorefining Catalyst	
Final Management	**Basis for Consideration in Risk Assessment**
Transfer metal catalyst for reclamation or regeneration	Not modeled, see discussion on previous page
Disposal offsite in Subtitle D landfill	Modeled
Disposal onsite in Subtitle D landfill	Modeled
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite recycle	Not modeled, exempt management practice

Table 3.3.11. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RCs**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfills[2,3]	5	6	0	3,048	—	37.25	2,250
All Management Practices Except Subtitle C Landfills[1,3]	—	71	0	18,436	—	88	500
	Onsite Landfill Characteristics						
	Surface Area (acres)				4.8	7.7	30
	Remaining Capacity (cu.yd.)				6,970	70,500	838,000
	Percent Remaining Capacity				2	3.5	80
	Total Capacity (cu.yd.)				82,300	85,500	840,000
	Number of Strata in Completed Unit				0	8	16
	Depth Below Grade (ft)				3	18	50
	Height Above Grade (ft)				0	1.5	12
	# of Landfills: 4						
	Aquifer Information						
	Depth to Aquifer (ft)				14	34.5	97
	Distance to Private Well (ft)				3,500	7,585	26,400
	Population Using Private Well				1	1	1
	Distance to Public Well (ft)				26,400	42,200	58,000
	Population Using Public Well				1,500	1,500	1,500
	# of Aquifers: 4						
	Source: Unreported Uppermost Lowermost Combination	Public 3 0 1 0	Private 1 1 1 1				
	Classification of Uppermost Aquifer: Current or potential source of drinking water (0) Not considered a potential source of drinking water (4)						

[1] The number of onsite landfills characterized in Table 3.3.11 is greater than indicated in Table 3.3.9, which focuses only on volumes generated in 1992. Table 3.3.11 incorporates data from all onsite landfills receiving catalyst in any year reported in the §3007 survey.
[2] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).
[3] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.3.3.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.3.12 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.

- Three record samples of spent hydrorefining catalyst were collected and analyzed by EPA. These spent catalysts represent the various types of applications and active metals used by the industry and are summarized in Table 3.3.13.

These samples are representative of two important feeds to hydrorefining units, heavy gas oil and diesel fuel. As discussed earlier, almost all hydrorefining reactors use Ni/Mo and/or cobalt/molybdenum, with slightly more using nickel/molybdenum. Both catalyst types are represented by the sampling.

All three samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. One of the samples was found to exhibit the toxicity characteristic for benzene (i.e., the level of benzene in this sample's TCLP extract exceeded the corresponding regulatory level). Two samples were found to exhibit the toxicity characteristic for arsenic. The high aluminum, molybdenum, nickel, and cobalt concentrations can be attributed to the catalyst make up: nickel\molybdenum or cobalt\molybdenum on alumina. A summary of the results is presented in Table 3.3.14. Only constituents detected in at least one sample are shown in this table.

At one refinery, the spent hydrorefining catalyst was collected by refinery personnel on supplied air because of high airborne arsenic concentration levels.

3.3.3.4 Source Reduction

All source reduction efforts and limitations tabulated for hydrotreating catalyst (Section 3.3.2.4) are applicable for hydrorefining catalyst.

Table 3.3.12. Hydrorefining Catalyst Physical Properties					
Properties	# of Values	# of Unreported Values	10th %	Mean	90th %
pH	53	71	4.9	6.7	9.2
Reactive CN, ppm	34	90	0	4.7	10
Reactive S, ppm	52	72	0.25	892	100
Flash Point, C	46	78	48.9	87	110
Oil and Grease, vol%	31	93	0	22	12.5
Total Organic Carbon, vol%	23	101	0	7.0	21
Specific Gravity	46	78	0.7	1.45	2.5
BTU Content, BTU/lb	13	111	0	1,684	4,700
Aqueous Liquid, %	54	70	0	3.6	17
Organic Liquid, %	50	74	0	1.0	3.75
Solid, %	92	32	83	97	100
Particle >60 mm, %	28	96	0	4	0
Particle 1-60 mm, %	47	77	50	89	100
Particle 100 μm-1 mm, %	36	88	0	6.7	25
Particle 10-100 μm, %	29	95	0	4.6	7.5
Particle <10 μm, %	26	98	0	0.3	0
Mean Particle diameter, microns	19	104	0	1,344	3,175

Table 3.3.13. Hydrorefining Catalyst Record Sampling Locations		
Sample number	Facility	Description: Type of Feed, Catalyst
R5-TC-01	Marathon, Garyville, LA	Heavy gas oil, Co/Mo catalyst
R7B-TC-01	BP, Belle Chasse, LA	Diesel, Ni/Mo catalyst
R21-RC-01	Chevron, Port Arthur, TX	Diesel, Co/Mo catalyst

Table 3.3.14. Residual Characterization Data for Spent Hydrorefining Catalyst

Volatile Organics – Method 8260A µg/kg

	CAS No.		R5-TC-01		R7B-RC-01		R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432		4,200		100,000		27,000	43,733	100,000	50,044	98,225	
n-Butylbenzene	104518	J	690	J	650		10,000	3,780	10,000	5,387	9,646	
sec-Butylbenzene	135988	J	940	J	510		5,300	2,250	5,300	2,650	5,136	
Ethylbenzene	100414	J	1,200		23,000	J	4,800	9,667	23,000	11,686	22,392	
Isopropylbenzene	98828	<	625		1,600	<	2,500	1,113	1,600	669	2,613	1, 2
p-Isopropyltoluene	99876	<	625	<	625		5,500	2,250	5,500	2,815	5,315	
Methylene chloride	75092	<	625	<	625	J	2,900	1,383	2,900	1,313	2,814	
Naphthalene	91203	<	625	J	960	J	2,900	1,495	2,900	1,226	2,832	
n-Propylbenzene	103651	J	900		2,000	<	2,500	1,450	2,000	778	3,143	1, 2
Tetrachloroethene	127184	<	625	<	625		9,500	3,583	9,500	5,124	9,163	
Toluene	108883		5,700		190,000		13,000	69,567	190,000	104,362	183,205	
1,2,4-Trimethylbenzene	95636		1,900		6,400		23,000	10,433	23,000	11,113	22,534	
1,3,5-Trimethylbenzene	108678	<	625		2,600		5,900	3,042	5,900	2,665	5,944	2
o-Xylene	95476		1,400		24,000		6,900	10,767	24,000	11,786	23,600	
m,p-Xylenes	108383 / 106423		4,100		78,000		23,000	35,033	78,000	38,391	76,837	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R5-TC-01		R7B-RC-01		R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	<	50	<	50	B	110	70	110	35	108	
Benzene	71432		110		4,200		160	1,490	4,200	2,347	4,046	
Ethylbenzene	100414	<	50		140	<	50	80	140	52	137	
Methylene chloride	75092	<	50	<	50		100	67	100	29	98	
Toluene	108883	<	50		4,000	<	50	1,367	4,000	2,281	3,850	
1,2,4-Trimethylbenzene	95636	<	50		180	<	50	93	180	75	175	
o-Xylene	95476	<	50		150	<	50	83	150	58	146	
m,p-Xylene	108383 / 10642	<	50		530	<	50	210	530	277	512	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R5-TC-01		R7B-RC-01		R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	<	165	<	1,650		370	268	370	145	583	1, 2
Benzo(g,h,i)perylene	191242		460	<	1,650	<	165	313	460	209	767	1, 2
Dibenzofuran	132649	<	165	J	1,100	J	220	495	1,100	525	1,066	
2,4-Dimethylphenol	105679	<	165		5,900		390	2,152	5,900	3,248	5,688	
Dimethyl phthalate	131113	<	165	<	1,650	J	250	208	250	60	338	1, 2
Di-n-butyl phthalate	87742	<	165	<	1,650	J	210	188	210	32	257	1, 2
2,4-Dinitrophenol	51285	<	800	<	8,000	J	370	370	370	NA	NA	1
2,4-Dinitrotoluene	121142	<	165	<	1,650	J	240	203	240	53	318	1, 2
Bis(2-ethylhexyl)phthalate	117817	<	165	<	1,650	J	110	110	110	NA	NA	1
Fluorene	86737	<	165	J	2,600		800	1,255	2,600	1,375	2,752	
Isophorone	78591	<	165	<	1,650	J	150	150	150	NA	NA	1
2-Methylchrysene	3351324		3,400	<	3,300	<	330	2,343	3,400	1,744	4,243	2
1-Methylnaphthalene	90120	J	520		8,600		2,900	4,007	8,600	4,152	8,528	
2-Methylnaphthalene	91576	<	165		12,000		5,100	5,755	12,000	5,945	12,228	2
2-Methylphenol	95487	<	165		5,600	J	260	2,008	5,600	3,111	5,396	
3/4-Methylphenol	NA	<	165	J	1,800	J	170	712	1,800	943	1,738	
Naphthalene	91203	<	165	J	3,000		580	1,246	3,000	1,531	2,916	
Phenanthrene	85018	<	165	J	2,200		1,200	1,188	2,200	1,018	2,296	2
Phenol	108952	<	165	J	1,800	<	165	710	1,800	944	1,738	
Pyrene	129000		3,300	J	1,600		640	1,847	3,300	1,347	3,313	2
Pyridine	110861	<	330	<	3,300		10,000	4,543	10,000	4,953	9,937	

HYDROREFINING CATALYST

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R5-TC-01	R7B-RC-01	R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl) phthalate	117817	3,100	< 50	J 18	1,056	3,100	1,770	2,984	
Carbazole	86748	< 100	< 100	J 17	17	17	NA	NA	1
2,4-Dimethylphenol	105679	< 50	220	J 30	100	220	104	214	
Dimethylphthalate	131113	< 50	< 50	J 34	34	34	NA	NA	1
1-Methylnaphthalene	90120	< 100	< 100	280	160	280	104	273	
2-Methylnaphthalene	91576	< 50	< 50	420	173	420	214	406	
2-Methylphenol	95487	< 50	290	J 70	137	290	133	282	
3/4-Methylphenol (total)	NA	< 50	150	J 65	88	150	54	147	
Naphthalene	91203	< 50	< 50	170	90	170	69	165	
Phenol	108952	JB 17	160	130	102	160	75	184	2

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R5-TC-01	R7B-RC-01	R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	270,000.0	80,000.0	170,000.0	173,333	270,000	95,044	276,825	2
Antimony	7440360	44.0	380.0	< 30.0	151.3	380.0	196.2	367.1	
Arsenic	7440382	100.0	650.0	730.0	493.3	730.0	343.0	866.8	2
Beryllium	7440417	43.0	< 0.5	< 2.6	15.3	43.0	24.0	41.4	
Cadmium	7440439	8.7	5.2	< 2.5	5.5	8.7	3.1	8.9	
Chromium	7440473	33.0	6.7	< 5.0	14.9	33.0	15.7	32.0	
Cobalt	7440484	18,000.0	8,700.0	24,000.0	16,900.0	24,000.0	7,709.1	25,294.3	2
Copper	7440508	46.0	17.0	32.0	31.7	46.0	14.5	47.5	2
Iron	7439896	730.0	470.0	1,100.0	766.7	1,100.0	316.6	1,111.4	2
Lead	7439921	1.3	< 0.3	2.8	1.5	2.8	1.3	2.8	
Molybdenum	7439987	74,000.0	25,000.0	77,000.0	58,666.7	77,000.0	29,194.7	90,456.3	2
Nickel	7440020	14,000.0	< 8.0	850.0	4,952.7	14,000.0	7,846.5	13,496.6	
Selenium	7782492	7.8	1.9	54.0	21.2	54.0	28.5	52.3	
Thallium	7440280	< 1.0	< 1.0	2.6	1.5	2.6	0.9	2.5	
Vanadium	7440622	31,000.0	130.0	< 25.0	10,385.0	31,000.0	17,853.2	29,825.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R5-TC-01	R7B-RC-01	R21-RC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	4.40	< 1.00	< 1.00	2.13	4.40	1.96	4.27	
Antimony	7440360	< 0.30	9.60	< 0.30	3.40	9.60	5.37	9.25	
Arsenic	7440382	0.23	34.00	6.90	13.71	34.00	17.69	33.19	
Cobalt	7440484	55.00	160.00	190.00	135.00	190.00	70.89	212.19	2
Iron	7439896	3.30	6.20	19.00	9.50	19.00	8.35	18.60	
Manganese	7439965	0.17	< 0.08	0.29	0.18	0.29	0.11	0.30	2
Molybdenum	7439987	< 1.00	13.00	17.00	10.33	17.00	8.33	19.40	2
Nickel	7440020	67.00	0.73	17.00	28.24	67.00	34.54	65.65	
Vanadium	7440622	3.30	< 0.25	< 0.26	1.27	3.30	1.76	3.16	
Zinc	7440666	0.39	< 0.10	< 0.10	0.20	0.39	0.17	0.38	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.

2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.

J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

ND Not Detected.

NA Not Applicable.

3.3.4 Catalyst from Sulfur Complex and H_2S Removal Facilities (Tail Gas Treating Catalyst) - Residual 8

3.3.4.1 Description

SCOT®-like tail gas treating catalyst is generated in a manner similar to hydrotreating catalyst. The unit's purpose is to convert SO_2 to H_2S. Units generating SCOT®-like tail gas treating catalyst include the following:

- SCOT®-like units
- Beavon reactors (as part of a Stretford system or as part of an amine system)

A process flow diagram of the tail gas unit, which includes the hydroprocessing reactor, is included with the discussion of sulfur catalyst in Section 3.9. Unlike hydrotreating and hydrorefining catalysts, catalysts in SCOT®-like units are not exposed to metals in the feed. Therefore, the poisoning mechanisms for tail gas catalyst are limited to carbon deposition.

When catalyst activity is unacceptable, the reactor is taken out of service and undergoes one or more of the following steps to reduce the hydrocarbon content of the reactor:

- Nitrogen sweep (to remove naphtha)
- Hydrogen sweep (to burn residual hydrocarbon)
- Oxidation (to burn residual hydrocarbon)

Catalyst Pretreatment Steps

Nitrogen sweep	29 facilities
Hydrogen sweep	9 facilities
Oxidation	22 facilities
No preparation	6 facilities
Other/unknown	6 facilities

Source: 54 facilities reporting *in situ* treatment information from RCRA §3007 questionnaire.

The vast majority of refineries uses cobalt/molybdenum on alumina catalyst. Based on a total of 69 SCOT®-like tail gas treating reactors reporting spent catalyst generation in the questionnaire, 93 percent reported using Co/Mo catalyst. An additional 6 percent reported using miscellaneous or unknown catalyst. This catalyst use profile is vastly different than other hydroprocessing applications where the usage of Ni/Mo and Co/Mo catalysts is roughly equal in the industry. Nickel catalyst is reported to be favored when denitrification reactions are desired (McKetta, 1992). Cobalt catalyst is likely to be used because only sulfur conversion is required for tail gas treating.

Approximately 83 MT of SCOT®-like catalyst generated in 1992 were identified as displaying hazardous characteristics. This is approximately 23 percent of the total quantity managed.

3.3.4.2 Generation and Management

1992 Identification of SCOT®-like Catalyst	
D001 (Ignitable)	66 MT
D003 (Reactive)	16 MT
Total identified as hazardous: 83 MT	

The spent catalyst is vacuumed or gravity-dumped from the reactors. Based on information from site visits, most refineries place the material directly into closed containers such as 55-gallon drums or flobins. The RCRA §3007 questionnaire data support these observations.

Twenty-one facilities reported generating a total quantity of 361 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "spent SCOT®-like catalyst" if they were assigned a residual identification code of "spent solid catalyst" or "solid catalyst fines" and were generated from a process identified as a SCOT® unit. These correspond to residual codes 03-A and 03-B, respectively, in Section VII.2 of the questionnaire and process code 15-D in Section IV-1.C of the questionnaire. Catalyst from other tail gas units, including Beavon-Stretford units, were not included in the statistics although the quantities of catalysts from the Beavon-Stretford units are similar to the quantities of catalyst generated from SCOT®-like units. Quality assurance was conducted by ensuring that all tail gas unit catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2. Based on the results of the questionnaire, approximately 65 facilities have SO_2 conversion reactors as part of their tail gas system (as the "front end" to their SCOT®, Stretford, or *Selectox* system) and thus likely generate spent tail gas hydroprocessing catalyst. Due to the infrequent generation of this residual, not all of these facilities generated spent catalyst in 1992. However, 1992 is expected to be a typical year in regard to catalyst change-out volume and management.

Table 3.3.15 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.3.15. Generation Statistics for Spent SCOT®-like Catalyst, 1992

Final Management	# of Streams	# of Streams with unreported volume	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Transfer metal catalyst for reclamation or regeneration	12	1	188	16	35 (estimate)
Disposal offsite in Subtitle C landfill	5	0	103	21	63
Disposal in offsite Subtitle D landfill	4	0	50	12	19
Disposal in onsite Subtitle D landfill	1	0	10	10	10
TOTAL	22	1	361	16	35

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the existing and possible "high potential exposure" disposal practices currently used. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.3.15 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practice is:

- Offsite Subtitle D landfilling (used for 14 percent of the total residual volume)

The input quantities for modeling releases using these scenarios were greater than those actually disposed in 1992. Instead, the management quantity is assumed to be the total quantity generated (minus that managed in Subtitle C units already). This is because other management methods, in particular reclamation, could change to landfilling in the future due to economic factors, convenience, or other factors. See Section 3.3.2.2 for additional details.

The management method accounting for the majority of the residual, transfer for offsite metals reclamation/regeneration, was not selected for modeling risks. A small number of catalyst reclaimers, such as CRI-MET in Louisiana and Gulf Metallurgical in Texas, reclaim spent catalyst for its vanadium, nickel, and molybdenum metal values. Both of these reclamation facilities routinely manage both characteristically hazardous and nonhazardous spent catalysts. One of these facilities segregates the hazardous and nonhazardous feedstocks, but following storage, both the hazardous and nonhazardous feeds are subjected to the same process. Therefore, risks from processing are equal for both characteristic and nonhazardous wastes.

A more detailed study of the catalyst recycling industry would be a significant endeavor, and was determined to be outside the scope of this listing determination. Based on the site visits described above, EPA believes that the practice of spent catalyst reclamation is valuable because it is consistent with the intent of RCRA and because, based on EPA's preliminary review of this industry, the spent catalysts appear to be managed and processed in a way that controls risks.

As with hydrotreating and hydrorefining catalysts, the Agency believed that it was unnecessary to model short-term interim storage used prior to final management. See the discussion for hydrotreating catalysts for details.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.3.16.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.3.17 provides a summary of the data for the targeted management practices used in the risk assessments for this residual. This table is developed using the RCRA §3007 survey of facilities reporting onsite landfilling of SCOT®-like catalyst in any reported year. The survey specified that if the residual was not generated in 1992, to provide the information for the last year the residual was generated.

Table 3.3.16. Selection of Risk Assessment Modeling Scenario: Spent SCOT®-like Catalyst	
Final Management	**Basis for Consideration in Risk Assessment**
Transfer metal catalyst for reclamation or regeneration	See discussion on previous page. Not modeled. Minimal volumes.
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal in offsite Subtitle D landfill	Modeled
Disposal in onsite Subtitle D landfill	Modeled
Onsite storage[1]	Not modeled, not final management practice

[1] Onsite storage indicates that the facility did not provide final management information.

3.3.4.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.3.18 summarizes the physical properties of the spent catalyst as reported in Section VII.A of the §3007 survey.
- Three record samples of spent SCOT®-like tail gas treating catalyst were collected and analyzed by EPA. These samples represent the spent catalyst generated throughout the industry and are summarized in Table 3.3.19.

Section 3.3.3.1 showed that there is essentially no process variation in the hydrotreating of tail gas. Essentially all catalyst is Co/Mo, and all treat sulfur recovery unit tail gas. Variations downstream of the unit, such as the type of treating solution used to remove H_2S, do not affect the spent catalyst generated in the hydroprocessing of this gas. Therefore, the sample set is expected to be representative of all tail gas catalyst generated.

All three samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. The high aluminum, molybdenum, and cobalt concentrations can be attributed to the catalyst make up: cobalt\molybdenum on alumina. A summary of the results is presented in Table 3.3.20. Only constituents detected in at least one sample are shown in this table.

Table 3.3.17. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RCs**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfills[2,3]	4	5	0	60	—	12.7	26
All Management Practices Except Subtitle C Landfills[1]	—	18	2	257	—	9.3	35
	Onsite Landfill Characteristics						
	Surface Area (acres)				3.65	17	30
	Remaining Capacity (cu.yd.)				62,800	450,400	838,000
	Percent Remaining Capacity				2	5	7
	Total Capacity (cu.yd.)				81,100	460,550	840,000
	Number of Strata in Completed Unit				0	0.5	1
	Depth Below Grade (ft)				3	27	50
	Height Above Grade (ft)				0	4.5	9
	# of Landfills: 2						
	Aquifer Information						
	Depth to Aquifer (ft)				18	28.5	39
	Distance to Private Well (ft)				8,970	8,970	8,970
	Population Using Private Well				No data	No data	No data
	Distance to Public Well (ft)				58,000	58,000	58,000
	Population Using Public Well				1,500	1,500	1,500
	# of Aquifers: 2						
	Source:		Public	Private			
	Unreported		1	1			
	Uppermost		0	1			
	Lowermost		1	0			
	Classification of Uppermost Aquifer: Not considered a potential source of drinking water (2)						

[1] The number of onsite landfills characterized in Table 3.3.17 is greater than indicated in Table 3.3.15, which focuses only on volumes generated in 1992. Table 3.3.17 incorporates data from all onsite landfills receiving spent catalyst in any year reported in the §3007 survey.

[2] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

[3] The mean and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream from one refinery may be disposed of in one management unit causing the 90th percentile number actually to be the sum of 2 or 3 waste volumes).

Table 3.3.18. SCOT®-like Catalyst Physical Properties					
Properties	# of Values	# of Unreported Values	10th %	Mean	90th %
pH	17	51	3.8	4.5	5.7
Reactive CN, ppm	13	55	0	24	20
Reactive S, ppm	21	47	1.0	38	112
Flash Point, C	12	56	60	84	100
Oil and Grease, vol%	9	56	0	0.3	1.0
Total Organic Carbon, vol%	10	57	0	0.6	2.5
Specific Gravity	18	50	0.7	1.75	2.56
BTU Content, BTU/lb	5	63	0	1,200	3,000
Aqueous Liquid, %	36	32	0	2.9	1.0
Organic Liquid, %	36	32	0	0.4	1.0
Solid, %	49	19	97.5	97	100
Particle >60 mm, %	20	48	0	15	100
Particle 1-60 mm, %	27	41	0	85	100
Particle 100 μm-1 mm, %	22	46	0	5.0	1.0
Particle 10-100 μm, %	18	50	0	0	0
Particle <10 μm, %	18	50	0.5	0	0
Mean Particle diameter, microns	7	59	0	2500	7,000

Table 3.3.19. SCOT®-like Catalyst Record Sampling Locations		
Sample number	Facility	Description: Catalyst
R5-SC-02	Marathon, Garyville, LA	Co/Mo catalyst
R7B-SC-01	BP, Belle Chasse, LA	Co/Mo catalyst
R11-SC-01	ARCO, Ferndale, WA	Co/Mo catalyst

3.3.4.4 Source Reduction

All source reduction efforts and limitations tabulated for hydrotreating catalyst (Section 3.3.2.4) are applicable for tail gas hydroprocessing catalyst.

In addition, some tail gas treating processes, such as the Stretford process, do not use solid catalyst and do not generate this residual. In the Stretford process, the catalyst is in a liquid state and is continuously reused. Stretford systems have limited use as tail gas units. Note that although the solid catalyst stream is eliminated in the Stretford process, the possibility of the liquid catalyst being present in other waste or residual streams was not investigated.

None of the samples exhibited any hazardous waste characteristics (i.e., no constituents in the samples' TCLP extracts exceeded the corresponding regulatory level, and no other characteristics of ignitability, corrosivity, or reactivity were found).

Table 3.3.20. Residual Characterization Data for Spent SCOT®-like Catalyst

Volatile Organics - Method 8260A µg/kg

	CAS No.	R5-SC-02	R7B-SC-01	R11-SC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432	< 5	< 625	60	33	60	39	117	1, 2
n-Butylbenzene	104518	< 5	J 700	< 25	243	700	396	674	
Trichlorofluoromethane	75694	29	< 625	< 25	27	29	3	33	1, 2
Toluene	108883	< 5	< 625	J 24	15	24	13	44	1, 2
1,2,4-Trimethylbenzene	95636	< 5	7,500	< 25	2,610	7,500	4,321	7,216	
1,3,5-Trimethylbenzene	108678	< 5	3,300	J 46	1,117	3,300	1,891	3,176	
o-Xylene	95476	< 5	J 1,040	J 24	356	1,040	592	1,001	
m,p-Xylenes	108383 / 106423	< 5	2,500	64	856	2,500	1,424	2,407	
4-Methyl-2-pentanone	108101	< 5	< 625	250	128	250	173	505	1, 2
Methyl ethyl ketone	78933	< 5	< 625	460	233	460	322	933	1, 2
Methylene chloride	75092	< 5	< 625	60	33	60	39	117	1, 2

TCLP Volatile Organics - Methods 1311 and 8260A µg/L

	CAS No.	R5-SC-02	R7B-SC-01	R11-SC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Methylene chloride	75092	< 50	< 50	B 1,600	567	1,600	895	1,541	

Semivolatile Organics - Method 8270B µg/kg

	CAS No.	R5-SC-02	R7B-SC-01	R11-SC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl)phthalate	117817	< 165	J 88	J 300	184	300	107	301	2
Di-n-butyl pthalate	84742	J 90	J 120	J 120	110	120	17	129	2

TCLP Semivolatile Organics - Methods 1311 and 8270B µg/L

	CAS No.	R5-SC-02	R7B-SC-01	R11-SC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis (2-ethylhexyl)phthalate	117817	540	< 50	JB 35	208	540	287	521	
Di-n-butyl phthalate	84742	< 50	< 50	J 31	31	31	NA	NA	1
Pyridine	110861	< 100	240	< 100	147	240	81	235	

Total Metals - Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R5-SC-02	R7B-SC-01	R11-SC-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	200,000	360,000	110,000	223,333.3	360,000.0	126,622.8	361,210.7	2
Antimony	7440360	14.0	20.0	< 6.0	13.3	20.0	7.0	21.0	2
Arsenic	7440382	< 10.0	< 20.0	28.0	19.3	28.0	9.0	29.2	2
Beryllium	7440417	< 0.5	2.9	< 0.5	1.3	2.9	1.4	2.8	
Cadmium	7440439	6.5	9.4	5.7	7.2	9.4	1.9	9.3	
Chromium	7440473	6.2	13.0	4.8	8.0	13.0	4.4	12.8	
Cobalt	7440484	13,000.0	19,000.0	11,000.0	14,333.3	19,000.0	4,163.3	18,866.7	
Copper	7440508	29.0	33.0	14.0	25.3	33.0	10.0	36.2	2
Iron	7439896	1,700.0	3,500.0	230.0	1,810.0	3,500.0	1,637.8	3,593.3	2
Manganese	7439965	3.2	54.0	< 1.5	19.5	54.0	29.8	52.1	
Molybdenum	7439987	48,000.0	54,000.0	25,000.0	42,333.3	54,000.0	15,308.0	59,001.9	2
Nickel	7440020	120.0	73.0	18.0	70.3	120.0	51.1	125.9	2
Selenium	7782492	2.2	< 2.5	< 0.5	1.4	2.2	1.2	4.0	1, 2
Sodium	7440235	1,300.0	< 600.0	2,500.0	1,433.3	2,500.0	1,006.6	2,529.5	2
Vanadium	7440622	260.0	210.0	72.0	180.7	260.0	97.4	286.7	2

SCOT CATALYST from SULFUR COMPLEX

	TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L							90% Confidence Interval	
	CAS No.	R5–SC–02	R7B–SC–01	R11–SC–01	Average Conc	Maximum Conc	Std Dev	Upper Limit	Comments
Aluminum	7429905	17.00	32.00	22.00	23.67	32.00	7.64	31.98	
Cadmium	7440439	< 0.03	0.20	< 0.03	0.08	0.20	0.10	0.19	
Chromium	7440473	< 0.05	0.13	< 0.05	0.08	0.13	0.05	0.13	
Cobalt	7440484	66.00	460.00	220.00	248.67	460.00	198.56	464.87	
Iron	7439896	6.30	< 0.50	< 0.50	2.43	6.30	3.35	6.08	
Manganese	7439965	0.34	0.99	< 0.08	0.47	0.99	0.47	0.98	
Molybdenum	7439987	39.00	480.00	430.00	316.33	480.00	241.48	579.27	2
Nickel	7440020	0.58	0.54	< 0.20	0.44	0.58	0.21	0.67	2
Vanadium	7440622	< 0.25	1.90	1.40	1.18	1.90	0.85	2.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.4 REFORMING

3.4.1 Process Description

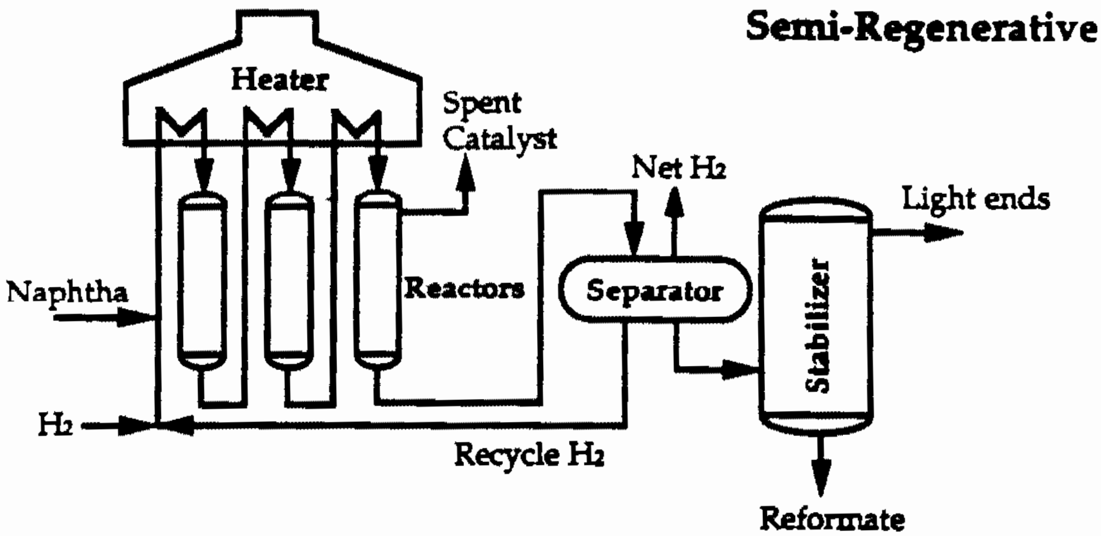
Catalytic reforming is used to upgrade (increase the octane of) naphtha for use as motor gasoline. Two types of reactions occur during the reforming step: (1) dehydrogenation of cycloparaffins to form aromatics, and (2) cyclization and dehydrogenation of straight chain aliphatics to form aromatics. In a reforming unit, several (typically 3 to 5) reactor vessels are placed in series interspersed with heaters. Catalyst is present in the reactor vessels and always contains platinum and in most cases, according to *Oil and Gas Journal*, is bimetallic (e.g., platinum/rhenium). Because the reaction is endothermic, heaters are required to maintain reaction conditions of approximately 150 psi and 500 to 1,000 °F (McKetta, 1992). Fractionators are used to separate the product reformate from light ends such as hydrogen, a reaction byproduct.

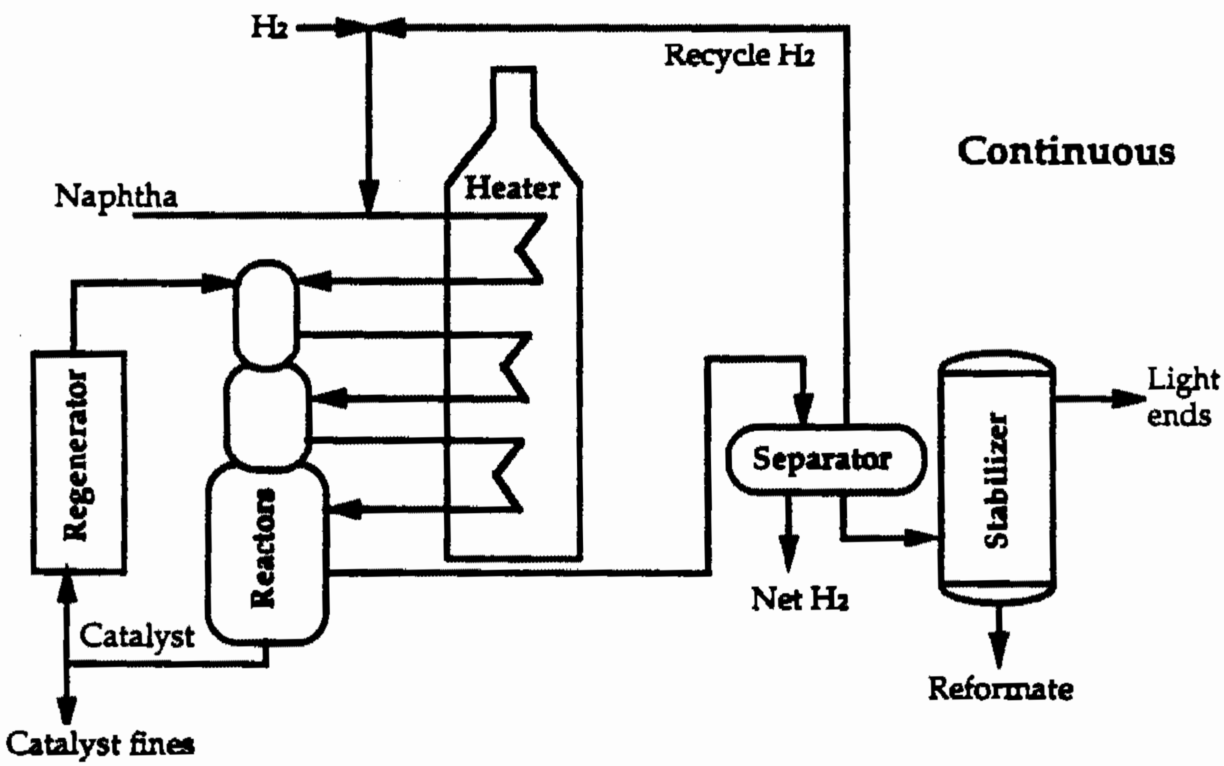
An important feed preparation step, hydrotreating, is not shown on the diagram. Sulfur is a reformer catalyst poison and for this reason the feed is desulfurized prior to entering the reformer beds; this catalyst is not considered reforming catalyst but is instead hydrodesulfurization (i.e., hydrotreating, see Section 3.3.1) catalyst.

Reforming unit operations are of three types: (1) semiregenerative, (2) cyclic, and (3) continuous, the principal difference being the period of time between catalyst regeneration. A semiregenerative unit consists of a series of reactors containing a fixed bed of catalyst. The unit typically operates for approximately 12 to 18 months before the unit is taken off-line for regeneration, when all reactors are regenerated at once and no product is generated. A cyclic unit also consists of a series of fixed bed reactors; one reactor is off-line at any one time for regeneration. In this way, the unit is always generating product from the three or four operating reactors. In a continuous unit, the catalyst continuously moves through the reactors at a slow rate, with regeneration in a (closed loop) parallel unit. According to RCRA §3007 data, 135 facilities have reformers. Sixty percent of the facilities have semiregenerative units, 25 percent have cyclic units, and 30 percent have continuous units. The summed percentages exceed 100 percent because some facilities have multiple units.

For all three cases, regeneration typically consists of (1) nitrogen purge, (2) oxygen burn, (3) addition of a chlorine source (such as a chlorinated hydrocarbon, hydrogen chloride, or elemental chlorine), and (4) nitrogen purge. The first nitrogen purge is used to remove free hydrocarbons from the reactor. The second step, addition of oxygen, burns off the built-up coke from the catalyst pellets. The third step, chlorination, is done to redistribute the platinum chloride on the alumina substrate to reactivate the catalyst following the oxygen burn. Some facilities may add a sulfur-containing compound after chlorination to passivate the catalyst somewhat. The final nitrogen purge is performed to prepare the catalyst bed for service. Figure 3.4.1 presents simplified diagrams of a semiregenerative and continuous process. The cyclic process closely resembles the semiregenerative process shown in this figure.

Figure 3.4.1. Process Flow Diagram for Catalytic Reforming





3.4.2 Reforming Catalyst - Residual 9

3.4.2.1 Description

Regeneration of a fixed catalyst bed can be performed only a limited number of times before the catalyst loses its activity. Complete removal of the catalyst and replacement with fresh catalyst occurs infrequently, such as every 5 to 10 years. To prepare the catalyst prior to dumping, the reactor may undergo one of the following steps to reduce the hydrocarbon content of the reactor:

- Nitrogen sweep (to remove naphtha)
- Hydrogen sweep (to burn residual hydrocarbon)
- Oxidation (to burn residual hydrocarbon)
- Steam stripping (to remove volatiles)

Catalyst Pretreatment Steps

Nitrogen sweep	73 facilities
Hydrogen sweep	64 facilities
Oxidation	61 facilities
No preparation	12 facilities
Steam stripping/ other/unknown	8 facilities

Source: 109 facilities reporting *in situ* treatment information from RCRA §3007 questionnaire.

Following removal, the catalyst may be shipped offsite in closed containers as spent catalyst. Alternatively, some facilities screen and replace the catalyst. This technique removes small particles of coke and catalyst. According to the RCRA §3007 questionnaire data, 5 facilities report this practice. Based on site visit information, this practice occurs more frequently than complete change-out (e.g., every 1 to 4 years). The purpose of screening is to prolong catalyst life and improve unit operation.

In the operation of the continuous catalytic reformer, catalyst fines are generated continuously and are typically removed prior to the regeneration step. Fines are generated from the movement of catalyst in the system. Following the reaction step, the catalyst must be blown to the top of the regenerator. Fines are collected because they are undesirable to the process.

1992 Identification of Reforming Catalyst

D018 (TC benzene)	419 MT
D003 (Reactive)	151 MT
D001 (Ignitable)	143 MT
D004 (TC Arsenic)	*16 MT*

Total identified as hazardous: 459 MT (some streams carry multiple codes)

In summary, residual reforming catalyst is generated primarily from three operations, in increasing order of generation frequency: (1) complete changeout of the catalyst (applicable for all three units); (2) periodic "dump and screen" (applicable for only the cyclic and semiregenerative units); and (3) continual generation of fines (applicable only for the continuous unit).

Approximately 459 MT of reforming catalyst generated in 1992 were identified as displaying hazardous characteristics. This is approximately 13 percent of the total volume managed.

3.4.2.2 Generation and Management

Based on the RCRA §3007 questionnaire and observations from 6 sampling events, catalyst is predominantly collected and stored in closed containers such as drums or flobins. This practice is conducted to minimize losses of this highly valuable residual.

Fifty-eight facilities reported generating a total quantity of 3,613 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "spent reforming catalyst" if they were assigned a residual identification code of "spent solid catalyst" or "solid catalyst fines" and were generated from a process identified as a reforming unit. These correspond to residual codes 03-A and 03-B, respectively, in Section VII.2 of the questionnaire and process code 08 in Section IV-1.C of the questionnaire. Quality assurance was conducted by ensuring that all reforming catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2. Based on the results of the questionnaire, 135 facilities use reforming units and thus likely generate spent reforming catalyst. Due to the infrequent generation of this residual, not all of these facilities generated spent catalyst in 1992. However, 1992 is expected to be a typical year in regard to catalyst change-out volume and management. Table 3.4.1 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

No plausible management scenario was selected by EPA to perform a risk assessment model. The predominant management method, offsite reclamation, was not modeled because of the absence of significant exposure pathways from the reclamation process. A more detailed study of the precious metals reclamation industry would be a significant endeavor, and was determined to be outside the scope of this listing determination. The predominant storage method, closed container, was not modeled because no releases or exposures are expected from a closed container.

No other management practice was assumed to be reasonable for this material. Based on facility estimates, the platinum value in the spent catalyst is roughly $25,000 to $50,000 per metric ton. In short, the residual is too valuable to be disposed or mishandled. In regard to other residuals generated during turnaround operation, such as support balls and fines that are not necessarily sent offsite for reclamation, these residuals are much smaller in volume (e.g., *de minimis* volumes) than their "parent" residuals and thus were not evaluated further.

Table 3.4.1. Generation Statistics for Spent Reforming Catalyst, 1992					
Final Management	**# of Streams**	**# of with unreported volume**	**Total Volume (MT)**	**Average Volume (MT)**	**90th % Volume (MT)**
Transfer metal catalyst for reclamation or regeneration	91	6	3,275	36	92 (estimate)
Offsite cement plant[1]	1	0	180	180	180
Onsite recycle[2]	7	1	90	13	64.3
Disposal in onsite wastewater treatment plant[1]	1	0	45	45	45
Offsite reuse	1	0	20	20	20
Onsite storage[3]	1	0	1.4	1.4	1.4
Disposal in onsite Subtitle D landfill[1]	1	0	0.5	0.5	0.5
Disposal offsite in Subtitle D landfill[4]	1	0	0.2	0.2	0.2
Other[5]	0	4	0	0	0
TOTAL	104	11	3,613	35	89

[1] These management methods reflect residuals derived from reforming catalyst: one facility generates crushed support balls from screening operations for disposal in an onsite landfill; one facility generates support balls from screening operations for offsite reuse at a cement plant; one facility generates wastewater from regeneration which is discharged to their wastewater treatment process.
[2] Onsite recycle includes reuse in same or similar unit, reuse as catalyst support, and onsite regeneration.
[3] Final, ultimate management was not provided for this residual following storage.
[4] This management method reflects a catalyst residual generated from a screening operation. These fines, containing platinum catalyst, coke, and support material, were disposed in an offsite landfill because the platinum value is too low for economic recovery.
[5] Other interim management practices were included, with no effect on total volume, 90th percentile, or mean volume.

3.4.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.4.2 summarizes the physical properties of the reforming catalyst as reported in Section VII.A of the §3007 survey.
- Six record samples of actual reforming catalyst were collected and analyzed by EPA. These spent catalysts represent the various types of generating processes used by the industry and are summarized in Table 3.4.3.

Table 3.4.2. Spent Reforming Catalyst Physical Properties					
Properties	**# of RC**	**# of Unreported Values**	**10th %**	**Mean**	**90th %**
pH	62	220	3.7	5.3	8
Reactive CN, ppm	36	246	0.1	9.6	10
Reactive S, ppm	46	236	0.5	75	500
Flash Point, C	48	234	0	83	200
Oil and Grease, vol%	47	235	0	1.0	1.0
Total Organic Carbon, vol%	41	241	0	1.4	5.5
Specific Gravity	57	225	0.51	2.6	2.6
BTU Content, BTU/lb	17	265	0	88	500
Aqueous Liquid, %	108	174	0	2.4	0
Organic Liquid, %	109	173	0	1.3	0.1
Solid, %	196	86	100	98	100
Particle >60 mm, %	37	245	0	19	100
Particle 1-60 mm, %	88	194	50	87	100
Particle 100 μm-1 mm, %	66	216	0	12.5	50
Particle 10-100 μm, %	34	248	0	3.1	0
Particle <10 μm, %	32	250	0	0.2	0
Mean Particle diameter, microns	23	257	0	2,100	2,720

Two samples of catalyst fines were collected from continuous catalytic reforming units, while the remaining four samples were collected from the "dumping" of fixed bed reactors (two samples were catalyst collected from cyclic units, and two samples were catalyst collected from semi-regenerative units). As discussed in Section 3.4.1, these units represent all of the catalytic reforming units. Each of the three units is common in the industry. Both platinum and bimetallic catalyst were collected, representing the two principal types of catalysts in use. No samples of fines collected from screened catalyst were collected. However, this is a low-volume stream in comparison to the reactor samples collected. These fines also contain many of the same constituents (i.e., platinum catalyst) and are often managed in the same way (i.e., offsite reclamation).

Table 3.4.3. Reforming Catalyst Record Sampling Locations		
Sample number	Facility	Description: Type of Generating Unit, Catalyst
R2-CR-01	Shell, Wood River, IL	Cyclic unit, platinum catalyst
R5-CR-01	Marathon, Garyville, LA	Continuous unit, platinum catalyst fines
R7B-CR-01	BP, Belle Chasse, LA	Semi-regenerative unit, platinum/rhenium catalyst
R11-CR-01	ARCO, Ferndale, WA	Semi-regenerative unit, platinum/rhenium catalyst
R14-CR-01	BP, Toledo, OH	Cyclic unit, platinum catalyst
R15-CR-01	Total, Ardmore, OK	Continuous unit, platinum/tin catalyst fines

All six samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. All samples were also analyzed for total dioxin/furans. One of the six samples analyzed displayed the TC characteristic for benzene (i.e., benzene levels in the TCLP extract were found above 0.5 mg/L). No other hazardous characteristics were displayed in any other samples. High aluminum concentrations can be attributed to the catalyst make up of platinum on alumina. A maximum concentration of 9.9 ng/kg (2,3,7,8-TCDD equivalence) was found in one sample. Dioxin is known to form in the reforming regeneration sequence, where chlorine is used as part of catalyst regeneration.[3] A summary of the results is presented in Table 3.4.4. Only constituents detected in at least one sample are shown in this table.

[3] EPA's Office of Water is investigating dioxin formation in reformers. For more information refer to the document *Petroleum Refining Industry - Presence of Dioxins and Furans in Wastewater Generated by Reforming Operations*. Ron Kirby, US EPA Office of Water, Engineering and Analysis Division, Energy Branch. May 1994.

Table 3.4.4. Residual Characterization Data for Spent Reforming Catalyst

Volatile Organics – Method 8260A µg/kg

	CAS No.	R2–CR–01	R5–CR–01	R7B–CR–01	R11–CR–01	R14–CR–01	R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432	< 25	J 1,000	2,300	430	570	26,000	5,054	26,000	10,291	11,255	
n–Butylbenzene	104518	< 25	57,000	220	< 25	< 22	8,900	11,032	57,000	22,795	24,768	
sec–Butylbenzene	135988	< 25	J 23,000	110	< 25	< 22	2,400	4,264	23,000	9,227	9,624	
Ethylbenzene	100414	< 25	51,000	1,900	< 25	620	26,000	13,262	51,000	21,099	25,975	
2–Hexanone	591786	< 25	J 23,000	< 25	< 25	< 22	< 625	3,954	23,000	9,334	9,578	
Isopropylbenzene	98828	< 25	27,000	180	< 25	46	5,700	5,496	27,000	10,773	11,988	
n–Propylbenzene	103651	< 25	60,000	570	< 25	85	< 625	10,222	60,000	24,388	24,917	
Toluene	108883	< 25	23,000	11,000	610	6,100	37,000	13,289	37,000	14,320	21,918	
1,2,4–Trimethylbenzene	95636	2,800	310,000	4,000	< 25	390	23,000	56,703	310,000	124,388	131,656	
1,3,5–Trimethylbenzene	108678	560	91,000	590	< 25	160	20,000	18,726	91,000	36,271	40,562	
o–Xylene	95476	110	110,000	5,100	< 25	720	49,000	27,493	110,000	44,705	54,430	
m,p–Xylenes	108383 / 106423	220	170,000	9,000	< 25	4,500	69,000	42,124	170,000	67,994	83,095	
Methyl ethyl ketone	78933	< 25	< 625	260	< 25	95	3,200	705	3,200	1,243	1,454	
Methylene chloride	75092	< 25	< 625	< 25	56	< 22	< 625	32	55	16	44	1
Naphthalene	91203	1,900	< 625	430	< 25	< 22	9,500	2,084	9,500	3,698	4,312	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R2–CR–01	R5–CR–01	R7B–CR–01	R11–CR–01	R14–CR–01	R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432	< 50	3,000	J 66	J 42	< 50	NA	646	3,000	1,316	1,546	
Ethylbenzene	100414	< 50	470	J 69	J 99	< 50	NA	148	470	181	272	
Toluene	108883	< 50	4,000	440	260	300	NA	1,010	4,000	1,677	2,160	
1,2,4–Trimethylbenzene	95636	110	610	140	300	< 50	NA	242	610	226	397	
1,3,5–Trimethylbenzene	108678	< 50	160	< 50	J 80	< 50	NA	78	160	48	111	
o–Xylene	95476	< 50	1,200	210	140	< 50	NA	330	1,200	491	667	
m,p–Xylene	108383/106423	< 50	1,500	340	500	140	NA	500	1,500	583	905	
Methylene chloride	75092	< 50	< 50	< 50	B 930	B 200	NA	256	930	382	518	
Naphthalene	91203	120	< 50	< 50	J 67	< 50	NA	67	120	30	88	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R2–CR–01	R5–CR–01	R7B–CR–01	R11–CR–01	R14–CR–01	R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Anthracene	120127	< 165	< 660	< 165	< 165	< 165	J 140	140	140	NA	NA	1
Bis(2–ethylhexyl)phthalate	117817	< 165	J 940	< 165	370	< 165	< 165	328	940	311	516	
Butyl benzyl phthalate	85687	< 165	J 310	< 165	< 165	< 165	< 165	189	310	59	225	
Di–n–butyl phthalate	87742	< 165	< 660	< 165	J 230	< 165	J 67	154	230	58	198	1
Benz(a)anthracene	56553	4,500	< 660	< 165	< 165	< 165	< 165	970	4,500	1,741	2,019	
Benzofluoranthene (total)	NA	8,300	< 660	< 165	< 165	< 165	< 165	1,603	8,300	3,287	3,584	
Benzo(g,h,i)perylene	191242	6,500	< 660	< 165	< 165	< 165	< 165	1,303	6,500	2,554	2,842	
Benzo(a)pyrene	50328	2,900	< 660	< 165	< 165	< 165	< 165	703	2,900	1,094	1,363	
Dibenz(a,h)anthracene	53703	J 260	< 660	< 165	< 165	< 165	< 165	184	260	42	213	1
2,4–Dimethylphenol	105679	< 165	15,000	< 165	< 165	< 165	< 165	2,638	15,000	6,056	6,287	
Chrysene	218019	4,000	< 660	< 165	< 165	< 165	< 165	887	4,000	1,538	1,813	
Fluoranthene	206440	5,000	< 660	< 165	< 165	< 165	< 165	1,053	5,000	1,944	2,224	
Fluorene	86737	< 165	< 660	< 165	< 165	< 165	J 78	78	78	NA	NA	1
Indeno(1,2,3–cd)pyrene	193395	4,600	< 660	< 165	< 165	< 165	< 165	987	4,600	1,761	2,060	
Isophorone	78591	< 165	< 660	650	< 165	< 165	< 165	262	650	217	411	1
1–Methylnaphthalene	90120	2,000	J 1,200	< 330	< 330	< 330	2,400	1,098	2,400	926	1,656	
2–Methylnaphthalene	91576	3,000	3,700	J 91	< 165	< 165	11,000	3,020	11,000	4,220	5,563	
2–Methylphenol	95487	< 165	25,000	J 270	< 165	< 165	3,300	4,844	25,000	9,952	10,841	
3/4–Methylphenol (total)	NA	< 165	24,000	330	< 165	< 165	4,500	4,888	24,000	9,520	10,624	
Naphthalene	91203	2,100	8,900	J 190	J 130	< 165	6,900	3,064	8,900	3,672	5,398	
Phenanthrene	85018	14,000	< 660	< 165	< 165	690	J 160	2,640	14,000	5,571	5,997	
Phenol	108952	< 165	21,000	< 165	< 165	< 165	2,600	4,043	21,000	8,364	9,083	
Pyrene	129000	4,200	< 660	< 165	< 165	< 165	< 165	920	4,200	1,619	1,898	
2–Methylchrysene	3351324	J 370	< 1,320	< 330	< 330	< 330	< 330	338	370	18	350	1

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TCLP Semivolatile Organics – Methods 1311 and 8270B µ/L

	CAS No.		R2–CR–01		R5–CR–01		R7B–CR–01		R11–CR–01		R14–CR–01		R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2–ethylhexyl)phthalate	117817	<	50	<	50	<	50	JB	61	<	50	<	50	52	61	4	55	
Di–n–butyl phthalate	84742	<	50	JB	15	<	50	J	48	<	50	<	50	32	48	23	62	1, 2
2,4–Dimethylphenol	105679	<	50		460	<	50	<	50	<	50	<	50	115	460	167	219	
1–Methylnaphthalene	90120	J	34	J	18	<	100	<	100	<	100	<	100	25	34	13	53	1, 2
2–Methylnaphthalene	91576	J	43	<	50	<	50	<	50	<	50	<	50	43	43	NA	NA	1
2–Methylphenol	95487	<	50		620	<	50	<	50	<	50	<	50	145	520	233	285	
3/4–Methylphenol (total)	NA	<	50		490	<	50	<	50	<	50	<	50	123	490	180	232	
Naphthalene	91203	J	59	J	27	<	50	<	50	<	50	<	50	49	59	11	54	
Phenanthrene	85018	J	35	<	50	<	50	<	50	<	50	<	50	35	35	NA	NA	1
Phenol	108952	<	50	B	380	<	50	<	50	<	50	<	50	105	380	135	186	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

			R2–CR–01		R5–CR–01		R7B–CR–01		R11–CR–01		R14–CR–01		R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905		230,900.0		180,000.0		460,000.0		290,000.0		150,000.0		190,000.0	250,000	460,000	113,666	318,492	
Antimony	7440360	<	12.0		17.0	<	6.0	<	6.0	<	6.0	<	6.0	6.3	17.0	4.7	11.6	
Arsenic	7440382	<	10.0		45.0	<	20.0	<	20.0	<	10.0		11.0	19.3	45.0	13.4	27.4	
Chromium	7440473		44.0		550.0		25.0		25.0		55.0		60.0	126.5	550.0	206.0	251.6	
Cobalt	7440484	<	10.0		2,900.0	<	6.0	<	5.0	<	6.0	<	5.0	486.3	2,900.0	1,181.5	1,200.3	
Copper	7440508	<	5.0		8,100.0		26.0		5.5	<	2.6		110.0	1,374.8	8,100.0	3,294.9	3,380.3	
Iron	7439896		460.0		51,000.0		2,100.0		120.0		500.0		5,400.0	9,930.0	51,000.0	20,215.9	22,111.6	
Lead	7439921	<	3.0		160.0	<	0.6		1.2		1.3	<	0.3	27.7	160.0	64.8	86.8	
Manganese	7439965	<	3.0		180.0		43.0	<	1.5	<	1.5		33.0	43.7	180.0	69.2	85.3	
Molybdenum	7439987	<	13.0		10,000.0		18.0		15.0	<	6.5		19.0	1,678.6	10,000.0	4,078.6	4,135.1	
Nickel	7440020	<	8.0		220.0		12.0		8.1	<	4.0		190.0	73.7	220.0	102.2	135.3	
Selenium	7782492	<	5.0		14.0	<	2.5	<	0.5	<	2.5	<	0.5	4.2	14.0	5.1	7.2	
Sodium	7440235	<	1,000.0		10,000.0	<	600.0	<	500.0	<	500.0	<	500.0	2,166.7	10,000.0	3,842.7	4,482.2	
Vanadium	7440622	<	10.0		78.0	<	25.0	<	5.0	<	6.0	<	5.0	21.0	78.0	28.0	37.9	
Zinc	7440666	<	4.0		2,900.0	<	2.0	<	2.0	<	2.0		20.0	486.3	2,900.0	1,181.5	1,200.3	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R2–CR–01		R5–CR–01		R7B–CR–01		R11–CR–01		R14–CR–01		R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905		28.00		5.30		360.00		340.00		94.00		23.00	141.72	360.00	164.24	240.66	
Chromium	7440473	<	0.05	<	0.05		0.19		0.23	<	0.05	<	0.05	0.10	0.23	0.08	0.15	
Cobalt	7440484	<	0.25		95.00	<	0.25	<	0.25	<	0.25	<	0.25	16.04	95.00	38.66	39.35	
Copper	7440508	<	0.13		61.00	<	0.13	<	0.13	<	0.13		0.31	10.30	61.00	24.84	25.27	
Iron	7439896	<	0.50	<	0.50		8.90		2.50		1.20	<	0.50	2.35	8.90	3.30	4.34	
Lead	7439921	<	0.02	<	0.02		1.10		1.70	<	0.02	<	0.02	0.48	1.70	0.74	0.92	
Manganese	7439965	<	0.08		1.90		1.60		0.50		0.20		0.66	0.83	1.90	0.75	1.28	
Nickel	7440020	<	0.20		0.72		0.65	<	0.20	<	0.20		3.60	0.91	3.60	1.33	1.73	
Selenium	7782492	<	0.03	<	0.03	<	0.03	<	0.03		0.06	<	0.03	0.03	0.06	0.01	0.04	
Zinc	7440666		0.52		99.00	<	0.10		0.30		0.50		0.25	16.78	99.00	40.28	41.05	

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Dioxins/Furans – Method 8290 ng/kg	CAS No.	R2–CR–01	R6–CR–01	R7B–CR–01	R11–CR–01	R14–CR–01	R15–CR–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
2,3,7,8–TCDF	51207319	12.00	< 0.29	< 0.21	< 0.18	< 0.55	< 0.16	2.23	12.00	4.70	5.11	
Total TCDF	55722275	100.00	< 0.29	< 0.21	< 0.18	6.90	< 0.16	32.95	100.00	76.98	79.34	
1,2,3,7,8–PeCDF	57117416	< 10.00	< 0.70	0.47	< 0.35	< 0.95	< 0.32	0.38	0.47	0.08	0.47	1
2,3,4,7,8–PeCDF	57117314	6.60	< 0.29	< 0.25	< 0.21	< 0.46	< 0.28	1.35	6.60	2.57	2.90	
Total PeCDF	30402154	150.00	0.91	0.47	< 0.35	< 0.95	< 0.32	25.50	150.00	60.99	62.25	
Total PeCDD	36088229	27.00	< 0.26	< 0.36	< 0.28	< 0.76	< 0.20	4.81	27.00	10.87	11.38	
1,2,3,4,7,8–HxCDF	70648269	24.00	< 0.28	< 0.25	< 0.14	< 0.65	< 0.25	4.26	24.00	9.67	10.09	
1,2,3,6,7,8–HxCDF	57117449	13.00	< 0.65	< 0.23	< 0.15	< 0.60	0.36	2.49	13.00	5.15	5.59	
2,3,4,6,7,8–HxCDF	60851345	< 2.70	< 0.31	< 0.39	0.31	< 0.76	0.41	0.35	0.41	0.05	0.40	1
1,2,3,7,8,9–HxCDF	72918219	8.70	< 0.70	< 0.35	< 0.17	< 1.00	< 0.32	1.87	8.70	3.36	3.90	
Total HxCDF	55684941	81.00	< 0.70	1.20	0.31	< 1.00	1.10	14.22	81.00	32.72	33.93	
Total HxCDD	34465468	20.00	< 0.55	< 0.75	< 0.70	< 1.60	< 0.32	3.96	20.00	7.66	8.72	
1,2,3,4,6,7,8–HpCDF	67562394	29.00	2.20	1.70	< 0.12	< 1.00	0.53	5.76	29.00	11.41	12.63	
1,2,3,4,7,8,9–HpCDF	55673897	18.00	< 0.49	< 1.30	< 0.24	< 1.00	< 0.21	3.54	18.00	7.10	7.82	
Total HpCDF	38998753	71.00	5.10	5.90	< 0.24	< 1.00	0.53	13.96	71.00	28.05	30.88	
1,2,3,4,6,7,8–HpCDD	35822469	26.00	8.90	6.40	< 0.22	2.20	0.44	7.36	26.00	10.51	13.69	
Total HpCDD	37871004	62.00	13.00	11.00	< 0.22	2.20	0.92	13.22	52.00	19.75	25.13	
OCDF	39001020	33.00	4.70	9.30	< 0.41	< 3.35	0.98	8.62	33.00	12.36	16.07	
OCDD	3268879	28.00	51.00	76.00	1.30	46.00	4.30	34.77	76.00	29.10	52.30	
2,3,7,8–TCDD Equivalence	1746016	9.90	0.15	0.19	0.03	0.07	0.09	1.74	9.90	4.00	4.15	

Comments:

1. Detection limits greater than the highest detected concentration are excluded from the calculations.
2. Upper Limit exceeds the maximum concentration.

Notes:

- B Analyte also detected in the associated method blank.
- J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit but greater than zero.
- ND Not Detected.
- NA Not Applicable.

3.4.2.4 Source Reduction

Like other catalysts, little can be done to reduce the volume of this residual. The catalyst will always, eventually, become inactive and require replacement. Efforts to decrease the frequency of generation or to decrease the toxicity of the generated residual appear to be the greatest opportunities for pollution prevention.

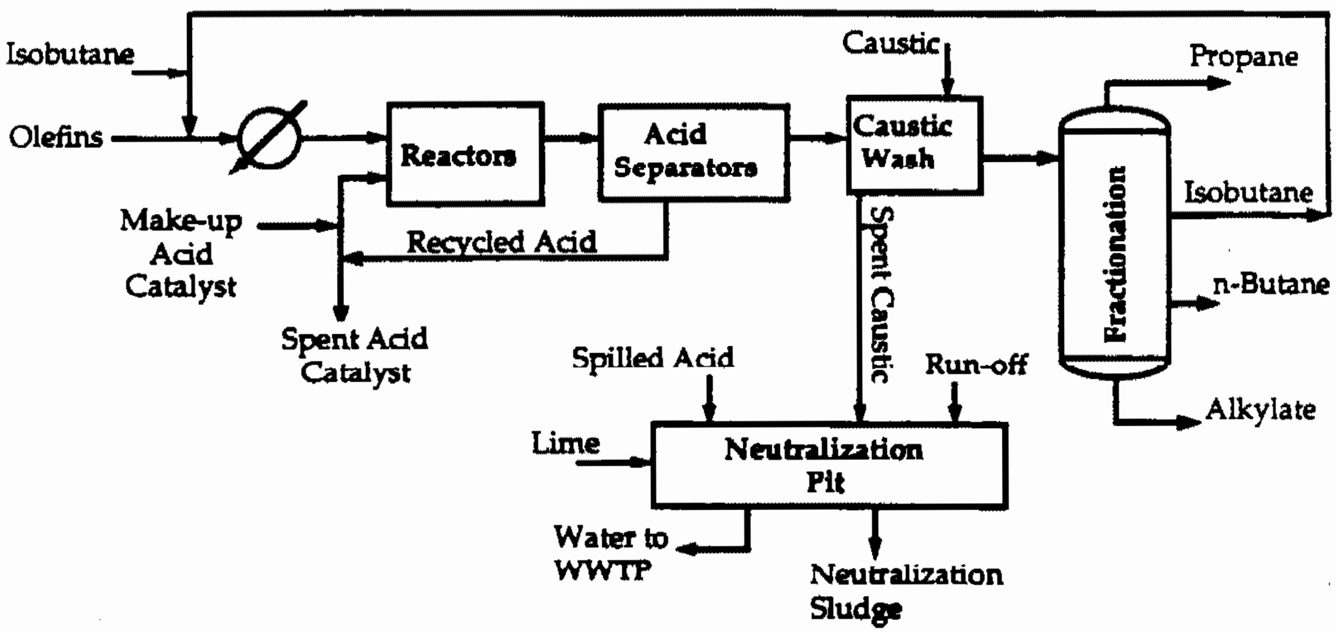
One refinery reported in its RCRA §3007 questionnaire that its reforming catalysts are now nonhazardous due to a new sweep procedure, reducing the facility's requirement to ship them as hazardous waste. Benzene and other light hydrocarbons are common contaminants in reforming catalyst. Another facility decreases the frequency of turnarounds by optimizing the feed. The quantity of material sent offsite can be reduced by separating the support material for onsite reuse. Many facilities perform this separation step already, but other techniques such as screening or air cyclones could be used to increase efficiency.

3.5 SULFURIC ACID ALKYLATION

3.5.1 Process Description

In the sulfuric acid alkylation process, olefin and isobutane gases are contacted over concentrated sulfuric acid (H_2SO_4) catalyst to synthesize alkylates for octane-boosting. The reaction products are separated by distillation and scrubbed with caustic. Alkylate product has a Research Octane Number in the range of 92 to 99. Figure 3.5.1 provides a generic process flow diagram for H_2SO_4 alkylation.

Figure 3.5.1. H_2SO_4 Alkylation Process Flow Diagram



The olefin stream is mixed with the isobutane and H_2SO_4 in the reactor. To prevent polymerization and to obtain a higher quality yield, temperatures for the H_2SO_4 catalyzed reaction are kept between 40 and 50°F (McKetta, 1992). Since the reactions are carried out below atmospheric temperatures during most of the year, refrigeration is required. Pressures are maintained so all reaction streams are in their liquid form. The streams are mixed well during their long residence time in the reactor to allow optimum reaction to occur.

The hydrocarbon/acid mixture then moves to the acid separator, where it is allowed to settle and separate. The hydrocarbons are drawn off the top and sent to a caustic wash to neutralize any remaining trace acid. The acid is drawn from the bottom and recycled back to the reactor. A portion of the acid catalyst is continuously bled and replaced with fresh acid to maintain the reactor's acid concentration around 90 percent. This spent H_2SO_4 is a residual of concern.

In 1992, DOE reported a U.S. alkylate capacity of 1,083,154 BPSD from 103 refineries (49 facilities used H_2SO_4 alkylation)

In the fractionator, the hydrocarbon streams are separated into the alkylate and saturated gases. The isobutane is recycled back into the reactor as feed.

Some facilities have neutralization tanks (in and above ground), referred to as pits, which neutralize spent caustic and any acid generated from spills prior to discharge to the WWTP, serving as surge tanks. Neutralizing agents (sodium, calcium, potassium hydroxides) are selected by the refineries. If necessary, the effluent to the pit is neutralized and, depending on the neutralizing agent, the precipitated salts form a sludge. This sludge is a residual of concern. Sludge may also be generated in process line junction boxes, in the spent H_2SO_4 holding tank, and during turnaround. However, due to the aqueous solubility of sodium, calcium, and potassium sulfates, sludge generation rates are relatively low and the majority of neutralization salts (e.g., sodium sulfate) are solubilized and discharged to the WWTP.

3.5.2 Spent Sulfuric Acid - Residual 10

3.5.2.1 Description

A slip stream of spent sulfuric acid is continuously drawn off the acid settler and replaced with fresh acid to maintain an acid strength of 90 to 92 percent. The spent acid, typically 100-300 tons per day, is either sent to an onsite acid plant for regeneration or, more commonly, sent offsite via tanker truck, railcar, or barge to a sulfuric acid supplier for reclamation.

Spent sulfuric acid used to produce virgin sulfuric acid, unless it is accumulated speculatively, is excluded from the definition of solid waste, as provided in Section 261.4(a)(7). The §3007 questionnaire results support the industry's claim that greater than 99 percent of the spent acid is reclaimed.

> According to the *Oil and Gas Journal*, growth in H_2SO_4 regeneration is expected through 1995 due to increased demand for alkylate, environmental pressures, and reformulation of gasoline.

The spent acid exhibits the RCRA characteristic for corrosivity. Currently, 17 facilities reported managing their spent acid as corrosive, which represents 251,199 MT of the waste. The Agency expects that all of this residual would fail the corrosivity characteristic if tested, however, due to the existing exemption, the characteristic does not apply and thus was not uniformly reported.

3.5.2.2 Generation and Management

The §3007 questionnaire responses indicated 1,760,071 MT of spent H_2SO_4 acid were generated in 1992. Residuals were assigned to be "spent sulfuric acid alkylation catalyst" if they were assigned a residual identification code of "spent liquid catalyst" and was generated from a process identified as a sulfuric acid alkylation unit. This corresponds to residual code 03-C in Section VII.2 of the questionnaire and process code 03-C in Section IV-1.C of the questionnaire. In this industry study, spent H_2SO_4 was the largest-volume waste being examined, twice the volume of the next largest-volume waste. Table 3.5.1 provides a description of the total quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

The RCRA §3007 questionnaire showed that spent H_2SO_4 is continuously drawn off the unit to either a holding tank, an onsite acid regeneration plant, or directly offsite to a reclaimer. At least 1,072,000 MT of sulfuric acid are managed in tanks.

Greater than 99 percent of the 1,760,071 MT of spent acid generated at 45 refineries is either used as replacement catalyst, regenerated onsite, or sent offsite for regeneration. Insignificant amounts of acid from spills are managed at the WWTP and discharged either to a POTW or to surface waters under a NPDES permit.

Table 3.5.1. Generation Statistics for Spent H_2SO_4 Alkylation Catalyst					
Final Management	**# of Streams**	**# with Unreported Volumes**	**Total Volume (MT)**	**Average Volume (MT)**	**90th % Volume (MT)**
Discharge to WWTP; discharge to surface waters; discharge to POTW	6	2	154.76	26	150
Offsite incineration	1	0	0.09	0.09	0.09
Reuse onsite as replacement catalyst	2	0	87,400	43,700	43,700
Transfer of acid for reclamation	38	1	1,424,162	37,478	74,414
Onsite acid regeneration/ onsite sulfuric acid plant	7	2	248,355	35,479	98,000
Total spent H_2SO_4	54	5	1,760,071	31,429	66,000

No plausible management scenarios for final management were identified for the use in the risk assessment due to the fact that the information collected in the §3007 survey supported the assumption that greater than 99 percent of the spent acid is reclaimed and, therefore, is covered by the existing exclusion. A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.5.2.

Table 3.5.2. Selection of Risk Assessment Modeling Scenario: Spent H_2SO_4 Alkylation Catalyst	
Waste	**Basis for Consideration in Risk Assessment**
Discharge to WWTP; discharge to surface waters; discharge to POTW	Not modeled, very small volume and existing coverage of current listings
Offsite incineration	Not modeled, *de minimis* volume
Reuse onsite as replacement catalyst	Not modeled, exempt management practice
Transfer of acid for reclamation	Not modeled, exempt management practice
Onsite acid regeneration/onsite sulfuric acid plant	Not modeled, exempt management practice

3.5.2.3 Characterization

Due to the pre-existing RCRA exclusion, residual characterization information was collected only in the §3007 survey and no record samples were collected for this residual of concern. Table 3.5.3 summarizes the physical properties of the tank sludge as reported in Section VII.A of the §3007 survey. One familiarization sample was collected and the characterization data for it is presented in Table 3.5.4.

Table 3.5.3. H_2SO_4 Alkylation Catalyst Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	35	29	1.0	2.23	3
Reactive CN, ppm	4	60	0	62.75	250
Reactive S, ppm	3	61	0	33.3	100
Flash Point, °C	10	54	60	103.9	183.6
Oil and Grease, vol%	4	60	0	3	8
Total Organic Carbon, vol%	8	56	0	3.3	5
Viscosity, lb/ft-sec	9	55	0.01	1.1	10
Specific Gravity	32	32	1.12	1.7	1.83
BTU Content, BTU/lb	3	61	0	233	700
Aqueous Liquid, %	43	21	100	84	100
Organic Liquid, %	37	27	0	5.3	10
Solid, %	34	30	0	3.1	2

Table 3.5.4. H_2SO_4 Alkylation Catalyst Familiarization Characterization Sample

Volatile Organics – Method 8260A µg/L

	CAS No.		B-SA-01
Acetonitrile	75058		55,000
Methylene chloride	75092	B	31,000
Methyl ethyl ketone	78933		35,000

Semivolatile Organics – Method 8270B µg/L

	CAS No.	B-SA-01
None Detected	NA	NA

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	B-SA-01
Aluminum	7429905	4.1
Arsenic	7440382	0.12
Calcium	7440702	15.9
Chromium	7440473	1.5
Copper	7440508	0.52
Iron	7439896	50.3
Manganese	7439965	0.33
Moylbdenum	7439987	0.60
Nickel	7440020	0.82
Sodium	7440235	37.5
Zinc	7440666	0.27

Miscellaneous Characterization

	B-SA-01
Corrosivity (pH)	<1

Notes:
B Analyte also detected in the associated method blank.
NA Not Applicable.

3.5.2.4 Source Reduction

> According to the *Oil and Gas Journal*, many refiners stated that, if a solid-acid process with economics comparable to sulfuric acid alkylation was available, they would consider it for new units.

Even though refiners recycle all of their spent H_2SO_4, they still are required to handle large quantities of acid. Transporting and handling these large volumes of spent acid poses significant potential risks due to transportation accidents and human error. Refiners and service companies are in the process of developing solid-acid catalysts to be used in the alkylation process.

Several solid-acid catalysts used for alkylation are being tested in pilot plants. The solid-catalyst reactor systems are different from the current liquid-acid systems, but for one solid-catalyst operation, the other process equipment is compatible. The three types of new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system).

3.5.3 Sludge from Sulfuric Acid Alkylation - Residual 11

3.5.2.1 Description

As discussed above, some facilities have neutralization pits, which neutralize streams headed to the WWTP, serving as surge tanks. Sludges occur from neutralizing salts (although most salts are soluble), settling polymer/tars, and dirt washed into process sewers. Sludge may also be generated in process line junction boxes, in the spent H_2SO_4 holding tank, and during turnarounds. Typical neutralizing agents include lime, sodium hydroxide, calcium chloride, and potassium hydroxide. Depending on the neutralizing agent (i.e., calcium hydroxide), precipitated salts form and settle to the bottom of the pit. These salts or sludges must be periodically cleaned out. Potassium and sodium sulfate salts are soluble in water, therefore, no sludges are generated.

Most refineries have switched from insoluble neutralizing agents (e.g., lime) to the soluble agents (e.g., sodium hydroxide, potassium hydroxide). The soluble sulfates do not create a sludge in the pits and are carried with the effluent to the WWTP. This practice has significantly reduced the amount of these sludges generated by refineries.

Two facilities reported managing their H_2SO_4 alkylation sludge as hazardous. These waste streams were managed either as F037 or as corrosive wastes.

3.5.2.2 Generation and Management

The questionnaire responses indicated 608 MT of H_2SO_4 alkylation sludge were generated in 1992. Residuals were assigned to be "sulfuric acid alkylation sludge" if they were assigned a residual identification code of "alkylation neutralization sludge" or "other process sludge" and was generated from a process identified as a sulfuric acid alkylation unit. These correspond to residual codes 02-B and 02-D, respectively, in Section VII.2 of the questionnaire and process code 09-A in Section IV-1.C of the questionnaire. Spent H_2SO_4 catalyst was mischaracterized as sludge in the 1983 RCRA survey and subsequent documents used to identify the consent decree wastes. The 1983 corrected data indicated only 482 MT of sludge was generated, not 61,338 MT. Table 3.5.5 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

The questionnaire responses reported that 17 MT of sludge were disposed of in either Subtitle D or C landfills in 1992. Approximately 380 MT of sludge were managed in land treatment units.

Table 3.5.5. Generation Statistics for H_2SO_4 Alkylation Sludge					
Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Transfer of acid for reclamation[1]	2	0	80	40	40
Disposal offsite Subtitle D landfill	2	1	10	5	10
Disposal offsite Subtitle C landfill	1	0	7	7	7
Discharge to WWTP; discharge to surface water	3	3	130	43	120
Offsite land treatment	1	0	100	100	100
Onsite land treatment	2	0	280	140	278
Offsite incineration	1	0	1	1	1
Total H_2SO_4 alkylation sludge	12	4	608	47	120

[1] Process upset sludge 80-95% acid.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.6.1 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite land treatment (46% of sludge)
- Offsite land treatment (16.4% of sludge)
- Offsite Subtitle D landfilling (about 2% of sludge)

An onsite monofill scenario was rejected because of the intermittent generation frequency, which is not typical of waste that tends to be monofilled. Similarly, the Agency did not model interim storage of sludge prior to final management. This residual is infrequently generated, and space and cost constraints create incentives for the refineries to minimize on-site storage.

The sludges managed in wastewater treatment systems were not chosen for evaluation in the risk assessment because these sludges will settle out in the primary treatment steps and are already listed as hazardous.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.5.6.

Characterization data for the management units and their underlying aquifers were reported in the §3007 survey. Table 3.5.7 provides a summary of the data for the targeted management practices used in the risk assessment.

Table 3.5.6. Selection of Risk Assessment Modeling Scenario: H_2SO_4 Alkylation Sludge

Final Management	Basis for Consideration in Risk Assessment
Transfer of acid for reclamation[1]	Not modeled, exempt management practice
Disposal offsite Subtitle D landfill	Modeled
Disposal offsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Discharge to WWTP; discharge to surface water	Not modeled. Minimal volume. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be captured by existing hazardous waste listings and further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Offsite land treatment	Modeled
Onsite land treatment	Modeled
Offsite incineration	Not modeled, *de minimis* volume

[1] Process upset sludge 80-95% acid.

Table 3.5.7. Management Practices Targeted for Risk Assessment							
H_2SO_4 Alkylation Sludge							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Offsite Subtitle D Landfill[1]	2	2	1	10	—	5	10
Offsite Land Treatment Unit	1	1	0	100	—	100	100
Onsite Land Treatment Unit[3]	1	2	0	280	—	280	280
	Characteristics						
	Surface Area (acres)				15	20.2	170
	Depth of Incorporation (in)				5	8	12
	Amount Applied (1992 MT)[2]				74.3	5,129	6,100
	Methods of Incorporation: Disking (3)						
	# of Land Treatment Units: 3						
	Aquifer Information						
	Depth to Aquifer (ft)				15	15	15
	Distance to Private Well (1000 ft)				25	25	25
	Population Using Private Well				0	0	0
	Distance to Public Well (ft)				—	—	—
	Population Using Public Well				—	—	—
	# of Aquifers: 3						
	Source: Public / Private Unreported: 3 / 2 Uppermost: — / 1						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (1) Not considered a potential source of drinking water (1) Unreported (1)						

[1] The mean and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream from one refinery may be disposed of in one management unit causing the 90th percentile number actually to be the sum of 2 or 3 waste volumes).
[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the alkylation sludge and not just the sludge alone.
[3] The number of onsite land treatment units characterized in Table 3.5.7 is greater than indicated in Table 3.5.5 which focuses only on volumes generated in 1992. Table 3.5.7 incorporates data from all onsite land treatment units receiving sulfuric acid alkylation sludge in any year reported in the §3007 survey.

3.5.2.3 Characterization

Due to changes in management practices (i.e., changing from an insoluble neutralizing agent to a soluble one), samples of neutralization pit sludges were very difficult to obtain. Sludges generated in junction boxes and spent H_2SO_4 tanks are accessible only during unit turnaround every 2 to 5 years. These stipulations made sample procurability very difficult during the time of the field study. The number of refineries chosen for record sampling was expanded to increase the availability of this residual, however, the newly targeted samples were never actually available.

Two sources of residual characterization were developed during the industry study:

- Table 3.5.8 summarizes the physical properties of the sludge as reported in Section VII.A of the §3007 survey.
- One sample of H_2SO_4 alkylation sludge was collected and analyzed by EPA. Sample location is expressed in Table 3.5.9. Table 3.5.10 provides the characterization data for this sampling effort.

Table 3.5.8. H_2SO_4 Alkylation Sludge Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	17	15	1.0	5.5	9.8
Reactive CN, ppm	3	29	0	1667	250
Reactive S, ppm	4	28	0	50	100
Flash Point, °C	6	26	43.9	84.4	200
Oil and Grease, vol%	10	22	0	1.6	3.6
Total Organic Carbon, vol%	7	25	0.04	6.6	25
Specific Gravity	10	22	1.0	8.5	36
BTU Content, BTU/lb	2	30	100	800	1,500
Aqueous Liquid, %	11	21	0	12.6	25
Organic Liquid, %	11	21	0	8.4	5
Solid, %	11	21	20	79	100

Table 3.5.10 provides the characterization data for this sample. Only constituents detected in at least one sample are shown in this table. The sludge sample exhibited the toxicity characteristic for chromium and the corrosivity characteristic.

Table 3.5.9. H_2SO_4 Alkylation Sludge Record Sampling Locations		
Sample number	Facility	Description: Type of Generating Unit, Catalyst
R8B-SS-01	Amoco, Texas City, TX	Neutralization sludge from H_2SO_4 alkylation unit and H_2SO_4 plant, dredged from pit

3.5.2.4 Source Reduction

As mentioned previously, most refineries have switched from insoluble neutralizing agents (e.g., lime) to the soluble agents (e.g., sodium hydroxide, potassium hydroxide). The soluble sulfates do not create a sludge in the pits and are carried with the effluent to the WWTP. This practice has significantly reduced the amount of these sludges generated by refineries.

Another practice that has reduced the amount of sludge generated is the reduction of the frequency and method of testing the acid strength. By reducing the frequency of testing acid concentration from once every 2 hours to twice a day, the amount of neutralizing agent needed and the amount of solids and acid tars accumulating on the pit bottom have been reduced, because the sample port purge volumes are reduced.

Table 3.5.10. H_2SO_4 Alkylation Sludge Characterization

Volatile Organics – Method 8260A µg/kg

	CAS No.		R8B-SS-01
Acetone	67641		7,000
Ethylbenzene	100414	J	150
Toluene	108883	J	160
1,2,4-Trimethylbenzene	95636	J	280
m,p-Xylenes	108383 / 106423	J	170
Naphthalene	91203	J	180

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R8B-SS-01
Acetone	67641		810
Methylene chloride	75092	B	200
Methyl ethyl ketone	78933		120

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R8B-SS-01
Bis(2-ethylhexyl)phthalate	117817		1,000
Di-n-butyl phthalate	84742	J	250
Benz(a)anthracene	56553	J	270
Benzo(g,h,i)perylene	191242	J	250
Benzo(a)pyrene	50328	J	190
Chrysene	218019	J	480
Fluorene	86737	J	210
Phenanthrene	85018	J	680
Pyrene	129000		2,200
1-Methylnaphthalene	90120	J	1,400
2-Methylnaphthalene	91576		2,200
2-Methylchrysene	3351324	J	340
Naphthalene	91203	J	290

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.		R8B-SS-01
1-Methylnaphthalene	90120	J	24
2-Methylnaphthalene	91576	J	31
Naphthalene	91203	J	30

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R8B-SS-01
Aluminum	7429905	1,100
Antimony	7440360	5.8
Arsenic	7440382	2.4
Barium	7440393	3.2
Cadmium	7440439	0.09
Calcium	7440702	16,000
Chromium	7440473	190
Cobalt	7440484	3.3
Copper	7440508	37.0
Iron	7439896	6,800.00
Lead	7439921	23.0
Magnesium	7439954	670
Manganese	7439965	45.0
Mercury	7439976	0.035
Molybdenum	7439987	1.7
Nickel	7440020	280
Potassium	7440097	200
Sodium	7440235	10,000
Vanadium	7440622	3.4
Zinc	7440666	58.0

SLUDGE from SULFURIC ACID ALKYLATION

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6B-SS-01
Aluminum	7429905	87.0
Calcium	7440439	430.0
Chromium	7440473	15.0
Copper	7440508	1.4
Iron	7439896	520.0
Lead	7439921	1.1
Magnesium	7439954	58.0
Manganese	7439965	3.7
Nickel	7440020	17.0
Zinc	7440666	4.0

Miscellaneous Characterization

	R6B-SS-01
Corrosivity (pH)	0.2
Reactivity – Total Releasable Sulfide (mg/kg)	61

Notes:

B Analyte also detected in the associated method blank.

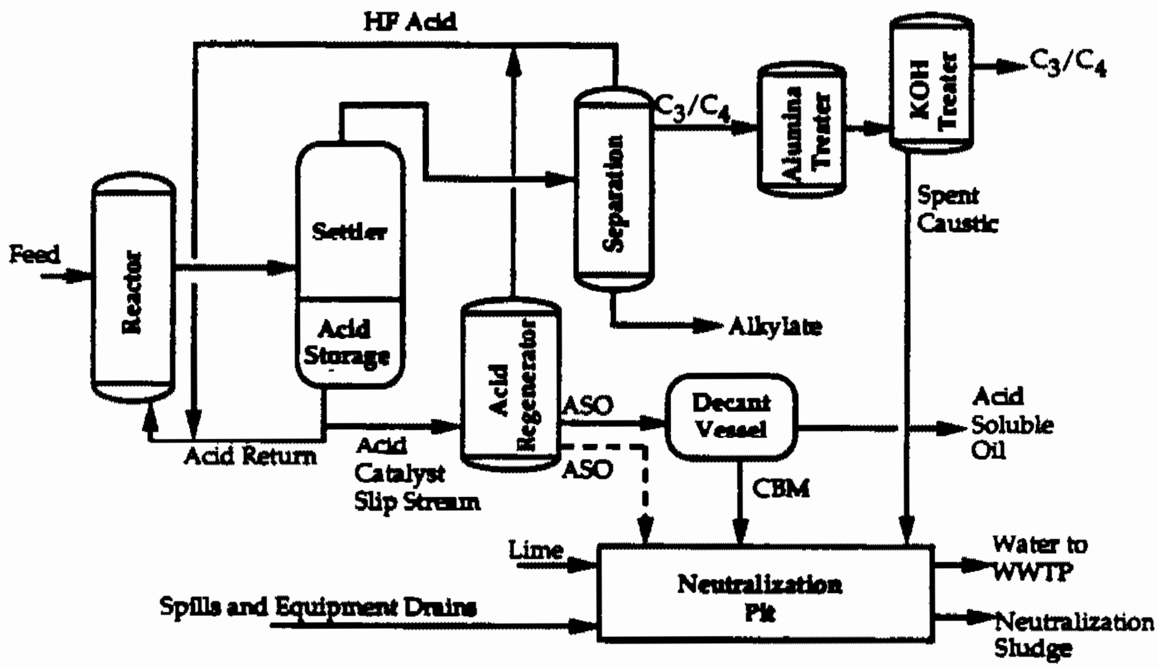
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

3.6 HYDROFLUORIC ACID ALKYLATION

3.6.1 Process Description

Hydrofluoric acid alkylation is very similar to the H_2SO_4 alkylation process. In the hydrofluoric acid alkylation process, olefin and isobutane gases are contacted over hydrofluoric acid (HF) catalyst to synthesize alkylates for octane-boosting. The reaction products are separated by distillation and scrubbed with caustic. Alkylate product has a research octane number (RON) in the range of 92 to 99. Because of its clean burning and contribution to reduced emissions, alkylate is a highly valued component in premium and reformulated gasolines. The HF process differs from the H_2SO_4 alkylation in that the HF catalyst is managed in a closed-loop process, never leaving the unit for replacement or regeneration. Figure 3.6.1 provides a generic process flow diagram for HF alkylation.

Figure 3.6.1. HF Alkylation Process Flow Diagram



The olefin stream is mixed with the isobutane and HF in the reactor. To prevent polymerization and to receive a higher quality yield, temperatures for the HF catalyzed reaction are maintained at approximately 100°F. Pressures are kept so all reaction streams are in their liquid form (usually 85 to 120 psi). The streams are mixed well in the reactor to allow optimum reaction to occur.

The hydrocarbon/acid mixture then moves to the settler, where it is allowed to settle and phase separate. The hydrocarbons are drawn off the top and sent to a fractionator. The acid is drawn from the bottom and recycled back to the reactor. A slip stream of acid is sent to an acid regenerator where distillation separates the HF acid from by-product contaminants. The HF acid from the regenerator is recycled back to the reactor. Fresh acid is added to replace acid losses at a rate of about 500 pounds per day.

> U.S. alkylation units are operating at more than 90% of the 1,083,154 BPSD capacity from 103 refineries (59 of which used HF alkylation), according to an Arthur D. Little report.

A residual of high molecular-weight reaction by-products dissolves in the HF acid catalyst and lowers its effectiveness. To maintain the catalyst activity, a slip stream of catalyst is distilled, leaving the by-product, acid soluble oil (ASO), as a residue. The ASO is charged to a decanting vessel where an aqueous phase settles out. The aqueous phase, an azeotropic mixture of HF acid and water, is referred to as constant boiling mixture (CBM). The ASO is scrubbed with potassium hydroxide (KOH) to remove trace amounts of HF and either recycled, sold as product (e.g., residual fuel), or burned in the unit's boiler. The CBM is sent to the neutralization pit. In some cases, the ASO from the regenerator is sent directly to the neutralization pit. The ASO is a residual of concern for the petroleum refining study.

A series of fractionators distills the feed streams from the reactor into the alkylate, saturated gases, and HF acid. The isobutane and HF are recycled back into the reactor as feed.

The main fractionator overhead is charged to the depropanizer and debutanizer, where high-purity propane and butane are produced. The propane and butane are then passed through the alumina treater for HF removal. Once catalytically defluorinated, they are KOH-treated and sent to LPG storage.

As HF is neutralized by aqueous KOH, soluble potassium fluoride (KF) is produced and the caustic is eventually depleted. Some facilities employ KOH regeneration. Periodically some of the KF-containing neutralizing solution is withdrawn to the KOH regenerator. In this vessel KF reacts with a lime slurry to produce insoluble calcium fluoride (CaF_2) and thereby regenerates KF to KOH. The regenerated KOH is then returned to the system, and the solid CaF_2 is routed to the neutralizing pit. The KF, at facilities that do not have a regenerator, is sent directly to the neutralizing pit, where it is reacted with lime to form a sludge.

Spent caustic, KOH scrubbers, acidic waters from acid sewers and, in some cases, CBM are charged to neutralization pits (in-ground tanks), which neutralize effluent to the WWTP. Neutralizing controls fluoride levels to the WWTP. Neutralizing agents (sodium, calcium, and potassium hydroxide) are selected based on the refineries' WWTP permits.

Effluent to the pit is neutralized, generally with lime, which forms a sludge (calcium fluoride) that collects on the bottom of the pit. This sludge is a residual of concern for the petroleum refining listing determination.

HF acid is an extremely corrosive and toxic chemical. Refineries go to great lengths to protect their personnel from coming in contact with HF. Prior to entrance to an HF alkylation unit, personnel must have special training and wear various levels of personal protective clothing (depending upon the work to be performed). The unit is generally cordoned off and marked as an HF hazard area. Valves, flanges, and any place where leaks can occur are painted with a special paint that will change colors when contacted with HF. The units are continuously monitored and alarms are activated if an HF leak is detected.

3.6.2 Sludge from Hydrofluoric Acid Alkylation - Residual 12

3.6.2.1 Description

As discussed above, the volume and type of sludge generated are dependant on the types of influents to the neutralization pit and the type of neutralizing agent used. Neutralizing agents are selected based on the fluoride limits in the WWTP permits. Generally, lime is used, creating calcium fluoride salts. The fluoride salts drop to the bottom of the pit and form a sludge, which periodically must be removed.

KOH scrubbers produce potassium fluoride, which is soluble. It is sent to the regenerator, as discussed above, or charged to the neutralization pit where it is contacted with lime. The calcium fluoride salt settles out, forming a sludge, and the resulting KOH solution is discharged to the WWTP. Some facilities discharge ASO or CBM to their neutralization pit, which adds heavy hydrocarbons (i.e., alkylation process tars) to their HF sludge.

The neutralization sludge, composed largely of calcium fluoride and unreacted lime, is removed on a batch basis approximately every 3 to 6 months. The sludge is usually removed using a vacuum truck. It may be dewatered using either a centrifuge, belt press, or plate and frame filter press prior to final management.

Seven HF sludge residuals were reported as being managed as hazardous. These residuals were managed as either F037, K051, ignitable and corrosive, or corrosive.

3.6.2.2 Generation and Management

The refineries reported generating approximately 11,288 MT of HF alkylation sludge in 1992. Residuals were assigned to be "HF alkylation sludge" if they were assigned a residual identification code of "alkylation neutralization sludge" and was generated from a process identified as an HF acid alkylation unit. This corresponds to residual code 02-B in Section VII.2 of the questionnaire and process code 09-B in Section IV-1.C of the questionnaire. Table 3.6.1 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.6.1. Generation Statistics for HF Alkylation Sludge					
Final Management	# of Streams	# of Unreported Volume Streams	Total Volume (MT)	Average Volume (MT)	90th Percentile Volume (MT)
Discharge to WWTP; discharge to surface water	3	1	78.6	26.2	28
Onsite land treatment	5	1	556	111	542
Offsite land treatment	1	0	686	686	686
Disposal offsite Subtitle D landfill	7	1	7,374.4	1,053.5	1,977
Disposal onsite Subtitle D landfill	1	0	45	45	45
Disposal offsite Subtitle C landfill	4	1	61	15	39
Disposal onsite surface impoundment[1]	1	0	221	221	221
Offsite industrial furnace[2]	1	0	828	828	828
Recovery onsite in coker	1	0	1,314	1,314	1,314
Neutralization	2	0	124	62	124
Total HF alkylation sludge	26	4	11,288	342	1,314

[1] Surface impoundment dedicated to alkylation unit; practice discontinued in 1992.
[2] Waste sent to cement kiln (applying for BIF status); refinery since closed.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.6.1 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Onsite land treatment (5% of sludge)
- Offsite Subtitle D landfilling (about 65% of sludge)
- Onsite Subtitle D landfilling (about 0.4% of sludge)

An onsite monofill scenario was rejected because of the intermittent generation frequency, which is not typical of waste that tends to be monofilled. Similarly, on-site interim storage was not modeled. The sludge is generated infrequently, and space and cost constraints create incentives for the refineries to minimize the on-site storage period.

The sludges managed in wastewater treatment systems were not chosen for evaluation in the risk assessment because these sludges will settle out in the primary treatment steps and are already listed as hazardous.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.6.2.

Table 3.6.2. Selection of Risk Assessment Modeling Scenario: HF Alkylation Sludge

Waste	Basis for Consideration in Risk Assessment
Discharge to WWTP; discharge to surface water	Not modeled. Minimal volume. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be captured by existing hazardous waste listings and further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Onsite land treatment	Modeled
Offsite land treatment	Modeled
Disposal offsite Subtitle D landfill	Modeled
Disposal onsite Subtitle D landfill	Modeled
Disposal offsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Disposal onsite surface impoundment	Not modeled, rare practice and unit closed in 1992
Offsite industrial furnace	Not modeled; rare practice; cement kiln managing hazardous waste and presently applying for BIF permit, and refinery reporting this practice is now closed
Recovery onsite in coker	Not modeled, management practice expected to be exempt

Characterization data for the management units and their underlying aquifers were reported in the §3007 survey. Table 3.6.3 provides a summary of the data for the targeted management practices used in the risk assessment.

Table 3.6.3. Management Practices Targeted for Risk Assessment							
HF Alkylation Sludge							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfill[1,4]	6	8	1	7,374.5	—	1,448	2,256.6
	Onsite Landfill Characteristics						
	Surface Area (acres)				7	7	7
	Remaining capacity (cu.yd.)				75,000	75,000	75,000
	Percent remaining capacity (cu.yd.)				13	13	13
	Total capacity (cu.yd.)				150,000	150,000	150,000
	Number of strata in completed unit				–	–	–
	Depth below grade (ft)				3	3	3
	Height above grade (ft)				5	5	5
	# of Landfills: 1						
	Aquifer Information						
	Depth to Aquifer (ft)				15.5	15.5	15.
	Distance to Private Well (ft)				16,000	16,000	16,000
	Population Using Private Well				–	–	–
	Distance to Public Well (ft)				–	–	–
	Population Using Public Well				–	–	–
	# of Aquifers: 1						
	Source: / Unreported / Uppermost / Lowermost / Combination	Public: 1 / – / – / –	Private: – / – / – / 1				
	Classification of Uppermost Aquifer: Not considered a potential source of drinking water (1)						

Table 3.6.3. Management Practices Targeted for Risk Assessment							
HF Alkylation Sludge							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Offsite Land Treatment Unit	1	1	0	686	—	686	686
Onsite Land Treatment Unit[1,3]	4	5	1	556	—	6.35	542
	Characteristics						
	Surface Area (acres)				0.6	7	32.3
	Depth of Incorporation (in)				4	12	60
	Amount Applied (1992 MT)[2]				2	229	1,049.5
	Methods of Incorporation: Disking (5) Subsurface Injection (1) Bulldozing (1)						
	# of Land Treatment Units: 7						
	Aquifer Information						
	Depth to Aquifer (ft)				15.5	60	150
	Distance to Private Well (ft)				2,000	6,200	26,400
	Population Using Private Well				1	2	3
	Distance to Public Well (ft)				2,000	10,240	18,480
	Population Using Public Well				250	250	250
	# of Aquifers: 6						
	Source: / Public / Private Unreported 3 6 Lowermost 2 1 Combination 2 --						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (1) Not considered a potential source of drinking water (6)						

[1] The mean and\or 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).

[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the HF acid alkylation sludge and not just the sludge alone.

[3] The number of onsite land treatment units characterized in Table 3.6.3 is greater than indicated in Table 3.6.1 which focuses only on volumes generated in 1992. Table 3.6.3 incorporates data from all onsite land treatment units receiving HF acid alkylation sludge in any year reported in the §3007 survey.

[4] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.6.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.6.4 summarizes the physical properties of the tank sludge as reported in Section VII.A of the §3007 survey.

- Five samples of HF alkylation sludge were collected from the neutralization pits. These sludges represent the various types of dewatering typically used by the industry. Table 3.6.5 presents sample locations and descriptions.

Table 3.6.4. HF Alkylation Sludge Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	31	16	7.5	10.27	12.6
Reactive CN, ppm	16	31	0	19.9	50
Reactive S, ppm	14	33	0	26.2	100
Flash Point, °C	14	33	60	83.65	100
Oil and Grease, vol%	13	34	0	2.68	5
Total Organic Carbon, vol%	8	39	0	3.41	10
Specific Gravity	15	32	1.1	1.18*	1.6
BTU Content, BTU/lb	2	45	100	1,050	2,000
Aqueous Liquid, %	34	13	0	54.6	90
Organic Liquid, %	27	20	0	1.44	5
Solid, %	35	12	10	49.4	100

* Used the 50th percentile because the arithmetic mean was higher than the 90th percentile due to an erroneous data point.

Samples of HF alkylation sludge were collected from the neutralization pits. Five samples were collected: four samples were dredged from the pit (not dewatered) and 1 sample was collected after it had been filter pressed (dewatered). The samples are believed to be representative of the sludge as generated. One of the dredged samples was dewatered by the laboratory prior to analysis at the request of the refinery to represent their "disposed" sludge. Table 3.6.6 provides a summary of the characterization data collected under this sampling effort. Only constituents detected in at least one sample are shown in this table. As presented in the data, 4 of the HF sludge samples exhibited the characteristic of corrosivity. High concentrations of calcium and sodium can be attributed to the neutralizing agents: lime, calcium hydroxide and sodium hydroxide.

Table 3.6.5. HF Alkylation Sludge Record Sampling Locations		
Sample Number	**Location**	**Description**
R3-HS-01	Exxon, Billings, MT	Dredged from neutralization pit
R8B-HS-01	Amoco, Texas City, TX	Dredged from neutralization pit
R9-HS-01	Murphy, Superior, WI	Dredged from neutralization pit
R15-HS-01	Total, Ardmore, OK	Dredged from neutralization pit
R7B-HS-01	BP, Belle Chasse, LA	Filter pressed

3.6.2.4 Source Reduction

As described in the H_2SO_4 alkylation section, several solid-acid catalysts used for alkylation are being tested in pilot plants. The reactor systems are different from the current liquid-acid systems, but for one system the other equipment is compatible. Three types of the new solid catalyst include aluminum chloride, alumina/zirconium halide, and antimony pentafluoride (a slurry system).

According to *Oil and Gas Journal*, solid-acid alkylation units are expected to have the greatest impact on HF alkylation capacity.

Recycling methods for the calcium fluoride include use in the steel-manufacturing industry. The calcium fluoride can be used as a neutral flux to lower the slag-melting temperature and to improve slag fluidity. CaF_2 can also be routed back to an HF acid manufacturer, as the basic chemical in the HF-manufacturing process, which is the reaction of H_2SO_4 with fluorspar to produce hydrogen fluoride and calcium sulfate (Meyers).

One refinery changed its neutralization pit from an in-ground tank to an above-ground tank to segregate the ASO from entering the pit and to prevent dirt and spilled hydrocarbons from contaminating the CaF_2. Their goal was to find a market to recycle the calcium fluoride. As of August 1994, the refinery had not found a market for the CaF_2 and was landfilling it.

Table 3.6.6. HF Alkylation Sludge Characterization

VolatileOrganics – Method 8260A µg/kg

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	< 12,500	8,300	16,000	2,600	6,100	9,140	16,000	5,208	12,710	
Benzene	71432	J 6,100	14,000	< 625	< 313	< 650	4,336	14,000	5,917	8,394	
Chlorobenzene	108907	< 12,500	1,800	< 625	< 313	< 650	847	1,800	654	1,382	1
n-Butylbenzene	104518	< 12,500	< 625	1,900	< 313	J 470	827	1,900	727	1,422	1
Crotonaldehyde	4170303	82,000	< 625	< 625	< 313	< 650	16,843	82,000	36,424	41,814	
sec-Butylbenzene	135988	J 20,000	< 625	< 625	J 290	< 650	4,436	20,000	8,701	10,403	
tert-Butylbenzene	98066	< 12,500	< 625	< 625	J 680	J 560	623	680	49	663	1
Ethylbenzene	100414	73,000	< 625	J 770	J 350	J 760	15,101	73,000	32,367	37,291	
Isopropylbenzene	98828	J 14,000	< 625	< 625	< 313	< 650	3,243	14,000	6,015	7,366	
p-Isopropyltoluene	99876	J 13,000	< 625	< 625	< 313	< 650	3,043	13,000	5,568	6,860	
Methyl ethyl ketone	78933	< 12,500	< 625	3,400	< 313	2,100	1,605	3,400	1,426	2,777	1
n-Propylbenzene	103651	67,000	< 625	< 625	< 313	J 660	13,849	67,000	29,713	34,219	
Toluene	108883	85,000	< 625	J 1,100	J 740	J 190	17,531	85,000	37,718	43,369	
1,2,4-Trimethylbenzene	95636	468,000	< 625	12,000	2,500	2,700	101,165	468,000	214,293	249,451	
1,3,5-Trimethylbenzene	108678	143,000	< 625	6,700	J 1,000	J 1,000	30,465	143,000	62,960	73,629	
o-Xylene	95476	127,000	< 625	1,800	J 220	J 410	25,971	127,000	56,479	64,692	
m p-Xylenes	108383/106423	352,000	< 625	3,700	J 460	J 1,200	71,597	352,000	156,755	179,065	
Naphthalene	91203	37,000	< 625	1,400	< 313	JB 980	8,064	37,000	16,181	19,157	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	< 50	760	1,300	260	3 530	584	1,300	486	917	
Benzene	71432	180	< 50	< 50	< 50	< 50	76	180	58	116	
Ethylbenzene	100414	B 530	< 50	< 50	< 50	< 50	146	530	215	293	
n-Propylbenzene	103651	120	< 50	< 50	< 50	< 50	64	120	31	85	
Toluene	108883	B 1,200	< 50	< 50	< 50	< 50	280	1,200	514	633	
Methylene chloride	75092	< 50	2,000	370	< 50	270	548	2,000	824	1,113	
Methyl ethyl ketone	78933	< 50	J 76	200	< 50	150	105	200	67	151	
1,2,4-Trimethylbenzene	95636	1,300	< 50	< 50	< 50	< 50	300	1,300	559	683	
1,3,5-Trimethylbenzene	108678	1,100	< 50	< 50	< 50	< 50	260	1,100	470	582	
o-Xylene	95476	B 1,100	< 50	< 50	< 50	< 50	260	1,100	470	582	
m,p-Xylene	108383/ 106423	B 480	< 50	< 50	< 50	< 50	136	480	192	268	
Naphthalene	91203	460	< 50	< 50	< 50	B 23	127	460	187	255	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl)phthalate	117817	J 2,100	< 1,000	< 5,157	< 2,063	< 165	1,332	2,100	930	2,094	1
Fluorene	86737	J 2,900	< 1,000	< 5,157	< 2,063	< 165	1,532	2,900	1,198	2,513	1
Indene	95136	J 3,300	< 1,000	< 5,157	< 2,063	< 165	1,632	3,300	1,356	2,743	1
Phenanthrene	85018	J 4,500	< 1,000	< 5,157	< 2,063	2,400	2,491	4,500	1,468	3,692	1
Phenol	108952	120,000	< 1,000	< 5,157	< 2,063	< 165	25,677	120,000	52,762	81,849	
1-Methylnaphthalene	90120	98,000	< 2,000	< 10,313	< 4,125	3,000	23,488	98,000	41,779	52,131	
2-Methylnaphthalene	91576	180,000	< 1,000	< 5,157	< 2,063	5,400	38,724	180,000	78,999	92,884	
2-Methylphenol	95487	18,000	< 1,000	< 5,157	< 2,063	< 165	4,877	18,000	6,499	9,332	
3/4-Methylphenol (total)	NA	32,000	< 1,000	< 5,157	< 2,063	< 165	8,077	32,000	13,506	17,337	
Naphthalene	91203	110,000	< 1,000	J 4,800	< 2,063	2,000	23,973	110,000	48,112	56,957	

HF ALKYLATION SLUDGE

TCLP Semivolatile Organics -- Methods 1311 and 8270B µg/L

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis(2-ethylhexyl)phthalate	117817	J 10	< 50	JB 13	< 50	JB 12	12	13	2	13	1
Di-n-butylphthalate	84742	< 50	< 50	< 50	< 50	B 120	84	120	31	85	
2,4-Dimethylphenol	105679	J 71	< 50	< 50	< 50	< 50	54	71	9	61	
2-Methylphenol	95487	830	< 50	< 50	< 50	< 50	206	830	349	445	
3/4-Methylphenol (total)	NA	1,200	< 50	< 50	< 50	< 50	280	1,200	514	633	
1-Methylnaphthalene	90120	J 97	< 100	J 21	< 100	J 19	46	97	44	94	1
2-Methylnaphthalene	91576	160	< 50	< 50	< 50	J 28	68	160	53	104	
Naphthalene	91203	320	< 50	< 50	< 50	J 22	98	320	124	184	
Phenol	108952	4,100	< 50	< 50	< 50	< 50	860	4,100	1,811	2,102	
Indene	95136	J 12	< 50	< 50	< 50	< 50	12	12	NA	NA	1

Total Metals -- Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	4,400.0	23.0	980.0	1,500.0	6,000.0	2,580.6	6,000.0	2,513.6	4,303.9	
Antimony	7440360	< 8.0	< 0.3	< 6.0	< 6.0	30.0	9.7	30.0	11.6	17.6	
Arsenic	7440382	5.7	0.2	< 1.0	< 5.0	5.3	3.4	5.7	2.6	5.2	
Barium	7440393	85.0	< 1.0	< 20.0	< 20.0	< 20.0	29.2	85.0	32.3	51.3	
Calcium	7440702	76,000.0	35,000.0	87,000.0	130,000.0	200,000.0	105,600.0	200,000.0	62,676.2	144,569.4	
Chromium	7440473	59.0	0.1	2.4	4.2	3.6	13.9	59.0	25.3	31.2	
Cobalt	7440484	710.0	< 0.3	< 5.0	< 5.0	< 5.0	145.1	710.0	315.6	361.6	
Copper	7440508	300.0	0.7	84.0	22.0	14.0	84.1	300.0	124.6	169.7	
Iron	7439896	26,000.0	26.0	720.0	2,200.0	570.0	5,903.2	26,000.0	11,253.3	13,625.1	
Lead	7439921	110.0	< 0.0	1.7	0.9	0.9	22.7	110.0	48.6	56.2	
Magnesium	7439954	3,700.0	83.0	1,100.0	1,200.0	< 500.0	1,316.6	3,700.0	1,408.0	2,281.9	
Manganese	7439965	180.0	1.0	33.0	34.0	8.7	51.3	180.0	73.4	101.7	
Nickel	7440020	730.0	4.1	220.0	78.0	57.0	217.8	730.0	297.2	421.6	
Potassium	7440097	4,100.0	< 25.0	< 500.0	34,000.0	< 500.0	7,825.0	34,000.0	14,723.8	17,910.3	
Selenium	7782492	5.6	< 0.025	< 0.5	< 0.5	< 0.5	1.4	5.6	2.3	3.0	
Sodium	7440235	8,600.0	19,000.0	4,100.0	4,300.0	14,000.0	10,000.0	19,000.0	6,447.1	14,420.0	
Vanadium	7440622	16.0	< 0.3	< 6.0	< 5.0	16.0	8.5	16.0	7.2	13.4	
Zinc	7440666	130.0	< 1.1	7.5	6.7	13.0	31.7	130.0	55.1	69.5	

TCLP Metals -- Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	< 1.00	< 1.00	< 1.00	< 1.00	5.20	1.84	5.20	1.88	3.13	
Antimony	7440360	< 0.30	< 0.30	< 0.30	< 0.30	0.62	0.36	0.62	0.14	0.46	
Calcium	7440702	570.00	< 25.00	< 25.00	< 25.00	2,000.00	529.00	2000.00	855.51	1115.52	
Copper	7440508	< 0.13	< 0.13	0.73	0.33	< 0.13	0.29	0.73	0.26	0.47	
Iron	7439896	3.70	< 0.50	< 0.50	2.80	< 0.50	1.60	3.70	1.54	2.66	
Manganese	7439965	0.71	< 0.06	< 0.06	0.64	0.32	0.36	0.71	0.30	0.57	
Nickel	7440020	< 0.20	0.40	0.46	4.30	0.50	1.17	4.30	1.75	2.37	
Potassium	7440097	150.00	< 25.00	< 25.00	1,600.00	< 25.00	365.00	1600.00	692.50	839.77	
Zinc	7440666	0.31	0.46	0.22	0.41	0.30	0.34	0.46	0.10	0.41	

Miscellaneous Characterization

	R3-HS-01	R8B-HS-01	R9-HS-01	R15-HS-01	R7C-HS-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Corrosivity (pH)	14	NA	13	13	13					
Total Fluorine (mg/kg)	160.0	NA	10,000.0	9,000.0	1.6	4,790.4	10,000.0	5,453.9	9,257.1	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.

2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.

J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

ND Not Detected.

NA Not Applicable.

3.7 THERMAL PROCESSES

3.7.1 Process Description

Thermal processes include all processes where feed is cracked solely by a thermal process, rather than a catalytic reaction mechanism. Like catalytic cracking processes such as FCC, thermal processes convert heavy stocks to light hydrocarbon products such as gasoline blending stocks. Unlike the FCC, however, thermal processes crack without a catalyst. The RCRA §3007 database identifies 64 facilities with thermal cracking processes, as follows (the total exceeds 64 because some facilities have multiple types of thermal processing units):

Process	Number of Facilities
Delayed coking	47
Visbreaking	10
Fluid coking	7
Thermal cracking	4
Coke calcining	2

3.7.1.1 Delayed Coking

A process flow diagram of a delayed coking unit is shown in Figure 3.7.1. Residuum is heated to the point of cracking, 900 to 950°F, and is continuously fed to a coke drum at 20 to 60 psi in the delayed coking unit (McKetta, 1992). The residuum cracks in the drum; the gaseous products exit the top of the drum and are recovered in the fractionation section. Coke, a product of the cracking process, slowly builds up in the drum.

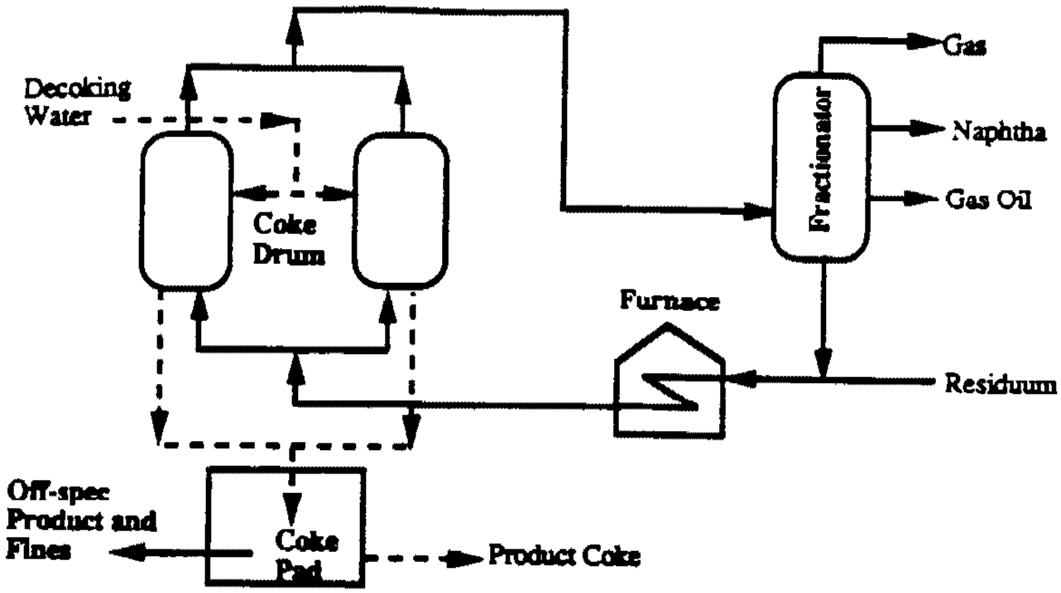
After approximately 24 hours, the coke drum fills with coke and the feed is switched to a parallel coke drum. The first drum is cooled and the built-up coke is hydraulically drilled out onto a pad and sold as a product.

The drilling cycle typically is as follows:

1. Feed to the coke drum is stopped.
2. The coke drum is depressurized and cooled; the offgases are vented to the recovery section.
3. The coke is drilled out using high pressure (3000 psi) water (McKetta, 1992).

Due to these repeated drilling cycles, the delayed coking process is a high consumer of water. Present refinery practice, however, includes the recycling of this water within the unit. To prepare the water for reuse and to collect additional coke product, the water is typically treated using gravity separation to remove fines. These fines are collected and typically mixed with the coke product.

Figure 3.7.1. Process Flow Diagram of Delayed Coking Unit



3.7.1.2 <u>Visbreaking</u>

The visbreaking process operates under less severe conditions than a coking process (850 to 900°F, 200 to 500 psi). Unlike delayed coking, the principal objective is not to produce gasoline blending stocks but instead to produce gas oil for use in heating oils. Residuum is fed to the reactor, where the feed is cracked and the overhead gases fractionated. Because the process is less severe, visbreaking units do not generate product coke or fines.

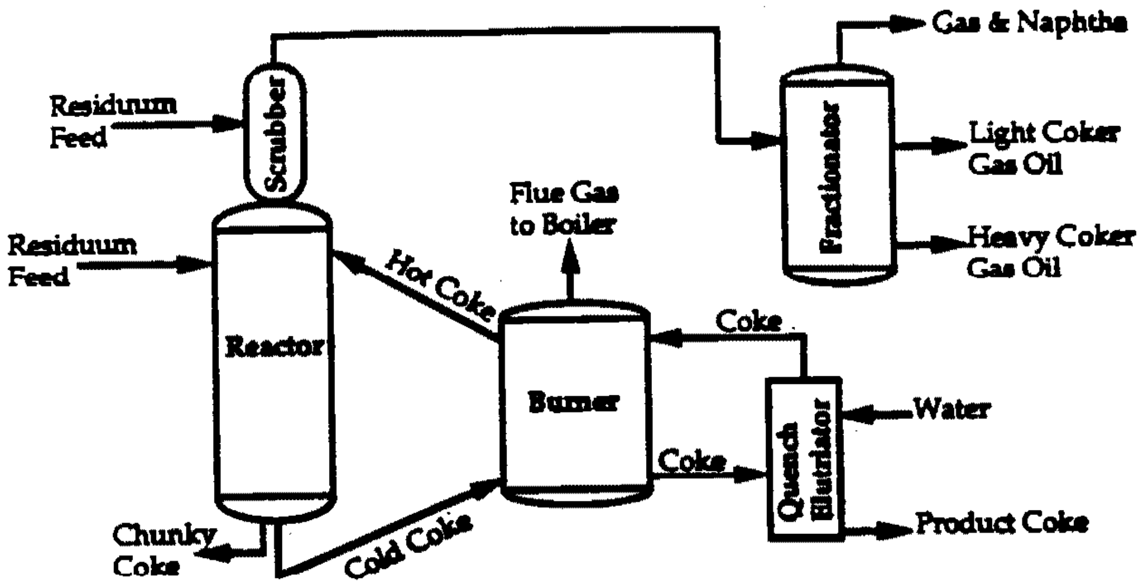
3.7.1.3 <u>Thermal Cracking</u>

Like visbreaking, thermal cracking operates under less severe conditions than delayed coking. Feed to the unit includes residuum and gas oils. The reaction is conducted at approximately 1000°F and 140 psi (Leffler, 1985). These conditions allow the heavier molecules to crack but prevent coke formation. A fractionator separates the products which include residual fuel oil, gasoline, and light gases such as butane. The Dubbs unit is a thermal cracking unit.

3.7.1.4 Fluid Coking

A process flow diagram of a fluid coking unit is shown in Figure 3.7.2. All fluid cokers presently operated in the U.S. are licensed by Exxon under the name fluid coking or flexicoking. Residuum is heated and pressurized to be continuously fed to a fluidized bed reactor. The process uses no catalyst. Rather, the reactor bed consists of fluidized coke fines. The residuum cracks in this reactor to form lighter hydrocarbons which are recovered overhead in a fractionator. Additional coke is formed from the reaction and is continuously removed from the bottom of the unit, where it is used as fuel for the unit or is sold as product.

Figure 3.7.2. Process Flow Diagram of Fluid Coking Unit



3.7.1.5 Coke Calcining

Facilities with delayed coking units may further process their coke in a calciner to upgrade the product. A calciner dries the material and removes volatile organic compounds. However, calcining was not considered part of the scope of this refining industry study because it is not inherent to the refining process.

3.7.2 Off-spec Product and Fines from Delayed Coking - Residual 13

3.7.2.1 Description

Of the five processes described above, only two generate RCs for this study:

- The delayed coking process generates product coke. When drilled out of the coke drum, the sizes of coke chunks range from 1 foot to one millimeter. The larger chunks are typically easily transferred to a coke product storage area, such as a pile. The smaller particles may become entrained in the coker unit water and are separated out by gravity, screening, or other physical separation processes. Fines may also appear near conveyer equipment. Some refineries do not distinguish fines from other coke product if they collect all of the coke in one storage area for sale. Most product, including fines, is sold as coke. Occasional product spillage results in the generation of off-spec product.

- The fluid coking process also generates product coke. Unlike the delayed coking process, the product is limited to fine, fluid-like particles. Larger agglomerated particles are sometimes formed and are removed from the system.

None of the other processes generate product coke, and therefore none generate "off-spec product" for the purposes of this listing determination. The only solid residuals typically generated from these processes are reactor clean-out wastes. These are likely to resemble coked particles and scale, and could not be considered "fines." Therefore, no other RCs are generated from thermal processing.

Approximately 744 MT of off-spec product and fines from thermal processes generated in 1992 were identified as displaying hazardous characteristics; less than 1 percent of the total volume managed.

1992 Identification of Off-spec Product and Fines from Thermal Processes
Total managed as hazardous (no specific designation): 744 MT

3.7.2.2 Generation and Management

Based on observations from engineering site visits, off-spec or fine coke from delayed coking is most often combined with other product coke for onsite interim storage in large piles.

Forty-four facilities reported generating a total quantity of 194,262 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "off-spec product and fines from thermal processes" if they were assigned a residual identification code of "off-spec product" or "fines" and were generated from a thermal process. These correspond to residual codes 05 and 06, respectively, in Section VII.2 of the questionnaire and process code 14 in Section IV-1.C of the questionnaire. Based on the results of the questionnaire, 53 facilities have delayed or fluid cokers and thus may generate off-spec or fine coke. The other 9 facilities likely either (1) did not generate a separate fines stream in 1992, or (2) combine all of their coke product, including fines, in one pile and did not account for size differences. Table 3.7.1 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on both (1) the Agency's past experience with risk assessment modeling in identifying pathways of greatest concern, and (2) actual management practices used to manage this residual in 1992. Based on these two selection criteria, the following management practices from Table 3.7.1 were identified as those likely to pose the greatest threats to human health and the environment:

- Offsite Subtitle D landfill (used for 3.6 percent of the total residual volume).

- Onsite Subtitle D landfill (used for 0.1 percent of the total residual volume).

The predominant management method, offsite sales, was not evaluated because of the difficulty of modeling exposure pathways from this non-petroleum refining industry. Based on observations from engineering site visits, off-spec or fine coke is most often combined with other coke onsite in a pile. EPA assessed risks only from waste management, not product storage. However, EPA did assess the potential for air releases during landfilling as a result of the frequent generation frequency and small particle size associated with this residual and believes that this assessment may be comparable to the potential risks associated with on-site storage prior to final management.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.7.2.

The management unit characterization data were provided in the §3007 survey. Table 3.7.3 provides a summary of the management unit characteristics and aquifer information.

3.7.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.7.4 summarizes the physical properties of the tank sludge as reported in Section VII.A of the §3007 survey.

- Six record samples of off-spec product or fines were collected and analyzed by EPA. These samples represent residuals generated from the two different types of units generating this residual and are summarized in Table 3.7.5.

Table 3.7.1. Generation Statistics for Off-Spec Product and Fines from Thermal Processes, 1992					
Final Management	# of Streams	# of with unreported volume	Total Volume (MT)	Average Volume (MT)	90th % Volume (MT)
Transfer with coke product[1]	38	9	168,986	4,447	17,000
Recovery onsite in coker[2]	2	1	9,358	4,679	9,125
Disposal in offsite Subtitle D landfill	11	0	7,064	642	441
Discharge to onsite WWTP[2]	6	1	4,996	833	3,200
Onsite boiler[2]	3	1	2,088	696	2,000
Disposal offsite in Subtitle C landfill	11	0	786	71	211
Onsite storage[3]	8	1	399	50	196
Offsite recycle to catalyst broker	1	0	200	200	200
Disposal in onsite Subtitle D landfill	3	0	187	62	164
Disposal in onsite Subtitle C landfill	2	0	140	70	70
Onsite land treatment	1	2	34	34	34
Offsite land treatment	1	0	21	21	21
Offsite incineration	2	0	3	1.5	1.5
Other[4]	1	5	0	0	0
TOTAL	90	20	194,262	2,158	5,372

[1] Management methods reported as "offsite use as fuel" and "transfer with coke product" were combined here because they were assumed to be the same.

[2] The facilities reporting the residual comprising the largest (90th percentile) volumes for using these management methods verified their management methods as follows:

- Onsite recovery in coker: offgas from fluid coking is sent to a CO boiler, then to an electrostatic precipitator (ESP). Fines from the ESP are recycled to the unit feed.
- Discharge to onsite wastewater treatment: Water discharged from the battery limits of this facility's delayed coking unit contains fines, which settle as primary sludge in their treatment system.
- Onsite boiler: offgas from fluid coking is sent to a CO boiler. Fines, present in the flue gas at the quantity indicated, are burned in this boiler.

[3] Storage onsite in piles and in roll-on/roll-off bins was reported as final management method; ultimate management was not provided.

[4] Other interim management practices were included, with no effect on total volume, a small effect on 90th percentile, and only a one percent effect on mean volume.

Table 3.7.2. Selection of Risk Assessment Modeling Scenario: Off-Spec Product and Fines from Thermal Processes	
Final Management	**Basis for Consideration in Risk Assessment**
Transfer with coke product[1]	Not modeled, exempt management practice
Recovery onsite in coker[2]	Not modeled, exempt management practice
Disposal offsite in Subtitle D landfill	Modeled
Discharge to onsite wastewater treatment[2]	Not modeled. Fines would settle out in sludge and be captured by existing hazardous waste listings. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Onsite boiler[2]	Not modeled, boiler is integral part of fluid coker (designed to control CO releases, not fines) and is not comparable to typical industrial boiler
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Onsite storage[3]	Not modeled; small volume and not final management practice
Offsite recycle to catalyst broker	Not modeled, exempt management practice
Disposal in onsite Subtitle D landfill	Modeled
Disposal in onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Onsite land treatment	Not modeled, rare practice, minimal volume; evaluated and emissions for landfill likely to be of greater concern
Offsite land treatment	Not modeled, less than 100 mt
Offsite incineration	Not modeled, *de minimis* volume

See footnotes for Table 3.7.1.

Table 3.7.3. Management Practices Targeted for Risk Assessment							
Off-spec Product/Fines from Thermal Processes							
Parameters	# of Fac.	# of RC	# RC w/ Unreported Volume	Total Volume (MT)	10th % Volume (MT)	50th % Volume (MT)	90th % Volume (MT)
Onsite and Offsite Subtitle D Landfill[1,2]	9	14	0	7,251	—	90.7	659
	Onsite Landfill Characteristics						
	Surface Area (acres)				12.6	36	50
	Remaining Capacity (thousand cu.yd.)				240	423	6,500
	Percent Remaining Capacity				0.7	1	100
	Total Capacity (thousand cu.yd.)				240	564	8,000
	Number of Strata in Completed Unit				400	400	400
	Depth Below Grade (ft)				0	0.5	1
	Height Above Grade (ft)				6	17	72
	# of Landfills: 3						
	Aquifer Information						
	Depth to Aquifer (ft)				16	32	166
	Distance to Private Well (ft)				5,280	5,280	5,280
	Population Using Private Well				0	0	0
	Distance to Public Well (ft)				5,280	5,280	5,280
	Population Using Public Well				--	--	--
	# of Aquifers: 3						
	Source: Unreported / Combination				Public: 3 / --	Private: 2 / 1	
	Classification of Uppermost Aquifer: Current or potential source of drinking water (1); Not considered a potential source of drinking water (2)						

[1] The 50th and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).

[2] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

Table 3.7.4. Off-spec Product/Fines from Thermal Processes Physical Properties					
Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	27	83	7.5	7.2	12.6
Reactive CN, ppm	17	93	0	4.5	50
Reactive S, ppm	20	90	0	18	100
Flash Point, C	34	76	60	125	100
Oil and Grease, vol%	23	87	0	7.4	5
Total Organic Carbon, vol%	21	89	0	53	10
Specific Gravity	43	67	1.1	1.26	1.6
BTU Content, BTU/lb	27	83	10	18,200	2,000
Aqueous Liquid, %	53	57	0	6.7	90
Organic Liquid, %	49	61	0	2.4	5
Solid, %	83	27	10	93	100
Particle >60 mm, %	26	84	0	12	100
Particle 1-60 mm, %	26	84	0	40	60
Particle 100 μm-1 mm, %	26	84	0	29	100
Particle 10-100 μm, %	25	85	0	19	0
Particle <10 μm, %	24	86	0	13	0
Mean Particle diameter, microns	12	97	0	8,545	500

The collected samples are expected to be representative of off-spec product and fines generated in the industry. Both fines from delayed coking and off-spec product from fluid coking were collected. These are the only two processes identified that generate the residual of concern. No samples of off-spec coke from delayed coking were collected; however, the composition differences between coke, fines, and off-spec coke are expected to be small because all are generated from the same coking drum.

All six samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. None of the TCLP extracts of any of the analyzed constituents exceeded corresponding regulatory levels. No samples were analyzed for any other characteristics (i.e., ignitability, corrosivity, reactivity); these samples were not expected to exhibit these characteristics. A summary of the results is presented in Table 3.7.6. Only constituents detected in at least one sample are shown in this table.

Table 3.7.5. Off-spec Product and Fines from Thermal Processes Record Sampling Locations

Sample number	Facility	Description: Type of Generating Unit
R6-TP-01	Shell, Norco, LA	Fines from delayed coking, from water settling
R8A-TP-01	Amoco, Texas City, TX	Fines from delayed coking, from water settling
R3B-TP-01	Exxon, Billings, MT	Off-spec product from fluid coking ("chunky coke")
R11-TP-01	ARCO, Ferndale, WA	Fines from delayed coking, from product conveyer dust collection
R12-TP-01	Texaco, Anacortes, WA	Fines from delayed coking, from water settling
R14-TP-01	BP, Toledo, OH	Fines from delayed coking, from spills collected in dumpster

3.7.2.4 Source Reduction

Some pollution prevention measures in the industry's delayed coking unit concern how to generate more, not less, of this residual. This is because most refineries blend their fines with their coke product for sale. In these cases, efforts include ways to keep the fines contained to the unit for ultimate recovery by mixing with coke product. These efforts include modifying drains or improving operations to limit the amount of fines in the water ultimately discharged to the wastewater treatment system. These fines can be collected with the product.

Table 3.7.6. Residual Characterization Data for Off-spec Product and Fines from Thermal Processes

Volatile Organics – Method 8260A µg/kg

	CAS No.	R6–TP–01	R6A–TP–01	R11–TP–01	R12–TP–01	R14–TP–01	R3B–TP–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzene	71432	< 5	< 25	1,500	< 625	< 23	< 625	467	1,500	587	821	
n–Butylbenzene	104518	< 5	82	< 625	2,200	J 18	< 625	593	2,200	839	1,098	
Ethylbenzene	100414	< 5	J 25	< 625	J 810	< 23	< 625	352	810	373	577	
p–Isopropyltoluene	99876	< 5	J 38	< 625	J 1,000	< 23	< 625	386	1,000	422	640	
n–Propylbenzene	103651	< 5	< 26	< 625	J 1,200	< 23	< 625	417	1,200	486	710	
Toluene	108883	< 5	J 19	2,600	< 625	< 23	< 625	683	2,600	1,079	1,333	
1,2,4–Trimethylbenzene	95636	< 5	270	< 625	8,200	63	< 625	1,631	8,200	3,229	3,577	
1,3,5–Trimethylbenzene	108678	< 5	140	< 625	2,900	J 30	< 625	721	2,900	1,104	1,388	
o–Xylene	95476	< 5	63	< 625	2,500	< 23	< 625	640	2,500	957	1,217	
m,p–Xylenes	108383 / 106423	< 5	93	1,600	3,200	< 23	< 625	924	3,200	1,271	1,690	
Naphthalene	91203	< 5	270	1,400	3,800	77	< 625	1,030	3,800	1,450	1,904	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R6–TP–01	R6A–TP–01	R11–TP–01	R12–TP–01	R14–TP–01	R3B–TP–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Methylene chloride	75092	< 50	< 50	< 50	B 340	B 290	JB 62	140	340	136	222	
Methyl ethyl ketone	78933	< 50	< 50	< 50	< 50	250	< 50	83	250	82	133	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R6–TP–01	R6A–TP–01	R11–TP–01	R12–TP–01	R14–TP–01	R3B–TP–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	< 825	< 4,126	< 1,030	11,000	< 825	< 165	2,995	11,000	4,163	5,503	
Anthracene	120127	1,900	J 2,700	J 1,400	J 9,400	J 1,600	< 165	2,861	9,400	3,308	4,854	
Benz(a)anthracene	56553	28,000	8,700	15,000	J 10,000	10,000	< 165	11,978	28,000	9,208	17,526	
Benzofluoranthene (total)	NA	28,000	J 6,100	10,000	J 5,100	4,800	< 165	9,028	28,000	9,811	14,940	
Benzo(g,h,i)perylene	191242	21,000	19,000	6,400	J 4,900	4,600	< 165	9,344	21,000	8,536	14,487	
Benzo(a)pyrene	50328	33,000	13,000	9,400	J 7,000	7,200	< 165	11,628	33,000	11,279	18,424	
bis(2–Ethylhexyl)phthalate	117817	< 825	< 4,125	87,000	< 5,157	< 825	< 165	16,349	87,000	34,670	37,241	
Carbazole	86748	6,900	< 8,250	J 2,400	J 5,000	< 1,650	< 330	3,258	6,900	2,655	5,076	1
Chrysene	218019	65,000	11,000	37,000	15,000	16,000	< 165	24,028	65,000	23,376	38,113	
Dibenz(a,h)anthracene	53703	14,000	J 3,000	6,600	J 2,600	< 825	< 165	4,532	14,000	5,154	7,637	
Dibenzofuran	132649	< 825	< 4,125	< 1,030	J 6,400	< 825	< 165	2,228	6,400	2,475	3,720	
7,12–Dimethylbenz(a)anthracene	57976	< 825	< 4,125	< 1,030	< 5,157	J 1,200	< 165	805	1,200	453	1,176	1
Fluoranthene	206440	3,600	< 4,125	J 2,000	J 4,300	J 1,200	< 165	2,565	4,300	1,700	3,590	
Fluorene	86737	J 900	< 4,125	< 1,030	14,000	J 550	< 165	3,462	14,000	5,354	6,688	
Indeno(1,2,3–cd)pyrene	193395	6,200	J 3,000	2,700	< 5,157	< 825	< 165	3,008	6,200	2,356	4,427	
Phenanthrene	85018	10,000	J 7,500	4,700	58,000	3,100	< 165	13,911	58,000	21,867	27,088	
Pyrene	1290000	27,000	14,000	5,600	14,000	4,700	< 165	10,911	27,000	9,594	16,692	
1–Methylnaphthalene	90120	J 890	J 4,400	J 430	58,000	J 1,100	< 330	10,858	58,000	23,144	24,804	
2–Methylnaphthalene	91576	3,400	J 8,200	J 1,600	89,000	3,600	< 165	17,694	89,000	35,036	38,806	
2–Methylchrysene	3351324	25,000	J 11,000	47,000	24,000	9,200	< 330	19,422	47,000	16,447	29,332	
Naphthalene	91203	3,100	J 2,900	J 1,900	12,000	J 1,600	< 165	3,611	12,000	4,242	6,167	

OFF-SPEC PRODUCT and FINES from THERMAL PROCESS

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R6-TP-01	R8A-TP-01	R11-TP-01	R12-TP-01	R14-TP-01	R3B-TP-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Di-n-butylphthalate	84742	JB 14	< 50	J 29	J 50	< 50	< 50	41	50	15	50	
Benz(a)anthracene	56553	< 50	< 50	J 13	< 50	< 50	< 50	13	13	NA	NA	1
Benzo(a)pyrene	50328	< 50	< 50	J 10	< 50	< 50	< 50	10	10	NA	NA	1
Bis(2-ethylhexyl) phthalate	117817	< 50	230	JB 40	J 20	< 50	< 50	75	230	77	121	
Chrysene	218019	< 50	< 50	J 35	< 50	< 50	< 50	35	35	NA	NA	1
2-Methylchrysene	3351324	< 100	< 100	J 15	< 100	< 100	< 100	15	15	NA	NA	1
1-Methylnaphthalene	90120	< 100	< 100	< 100	J 21	< 100	< 100	21	21	NA	NA	1
2-Methylnaphthalene	91576	< 50	< 50	< 50	J 23	< 50	< 50	23	23	NA	NA	1
Phenol	108952	JB 17	< 60	< 60	< 50	< 60	< 50	17	17	NA	NA	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R6-TP-01	R8A-TP-01	R11-TP-01	R12-TP-01	R14-TP-01	R3B-TP-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	84.0	87.0	< 20.0	130.0	< 20.0	< 20.0	56.8	130.0	45.6	84.3	
Chromium	7440473	< 1.0	< 1.0	< 1.0	3.0	< 1.0	< 1.0	1.3	3.0	0.8	1.8	
Copper	7440508	< 2.5	< 2.5	< 2.5	13.0	5.1	< 2.5	4.7	13.0	4.2	7.2	
Iron	7439896	230.0	190.0	50.0	600.0	370.0	< 10.0	275.0	600.0	288.0	448.5	
Lead	7439921	2.5	0.8	< 0.3	1.1	3.7	< 0.3	1.5	3.7	1.4	2.3	
Manganese	7439965	< 1.5	< 1.5	< 1.5	7.0	< 1.5	< 1.5	2.4	7.0	2.2	3.8	
Mercury	7439976	< 0.05	< 0.05	0.0283	0.11	< 0.05	< 0.05	0.06	0.11	0.03	0.07	
Nickel	7440020	46.0	12.0	34.0	15.0	120.0	8.5	39.3	120.0	42.1	64.6	
Selenium	7782492	< 0.5	< 0.5	1.4	< 0.5	< 0.5	< 0.5	0.7	1.4	0.4	0.9	
Vanadium	7440622	61.0	70.0	110.0	78.0	310.0	28.0	109.5	310.0	101.7	170.8	
Zinc	7440666	7.8	7.5	6.6	20.0	13.0	< 2.0	9.5	20.0	6.2	13.2	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6-TP-01	R8A-TP-01	R11-TP-01	R12-TP-01	R14-TP-01	R3B-TP-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Iron	7439896	< 0.50	< 0.50	< 0.50	1.40	< 0.50	< 0.50	0.65	1.40	0.37	0.87	
Lead	7439921	< 0.015	< 0.015	< 0.015	< 0.015	0.03	< 0.015	0.02	0.03	0.01	0.02	
Mercury	7439976	0.000334	0.000378	0.000588	0.000398	< 0.005	0.000308	0.000401	0.000588	0.000111	0.000477	1
Zinc	7440666	0.75	0.31	0.74	0.37	0.30	< 0.10	0.43	0.75	0.26	0.59	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

Notes:

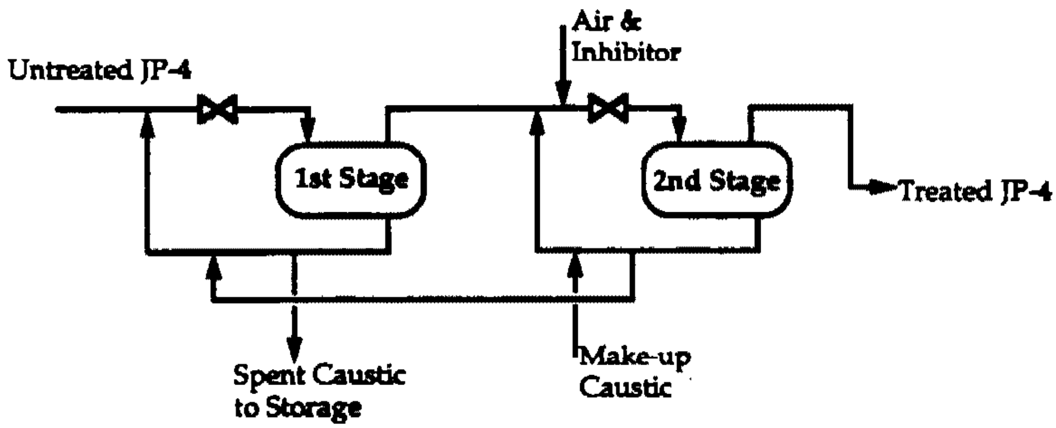
B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.8 LIQUID TREATING

3.8.1 Process Description

Liquid treating processes, for the purposes of this investigation, are synonymous with caustic treating. The purpose of caustic treating is to remove sulfur compounds such as mercaptans, H_2S, and phenolic sulfur compounds. Caustic treating of FCC fractions also removes cresylic acids, while treating jet fuel derived from certain crudes (such as some Delta, Venezuelan, Russian crudes) also removes naphthenic acids. Liquid treating consists of the countercurrent flow of the untreated light distillate with a solution of 5 to 20 percent caustic. The caustic can be regenerated to a certain degree by steam stripping or air contacting. In addition to regeneration, make-up caustic is required to maintain the effectiveness of the system. Figure 3.8.1 provides a generic process flow diagram for H_2SO_4 alkylation. The industry also employs oxidative caustic treating, which converts mercaptans to disulfides (which remain in the treated product) (McKetta).

Figure 3.8.1. Liquid Treating Process Flow Diagram



3.8.2 Spent Caustic - Residual 14

3.8.2.1 Description

A slip stream of spent caustic is continuously drawn off the caustic treater and replaced with fresh caustic to maintain caustic strength of 5 to 20 percent. The spent caustic is either sent offsite via tanker truck, railcar, or barge to Merichem for reclamation, discharged to the refinery's wastewater treatment system (sometimes for pH control), or reused in some way in the refinery's processes (e.g., FCC wet gas scrubbers, recovery of ammonia in sour water systems, makeup for desalter water, or reuse in a treating unit).

The spent caustic exhibits the RCRA characteristic for corrosivity. Currently, 54 facilities reported managing their spent caustic as hazardous, reporting primarily corrosivity, but also ignitability, reactivity and TC benzene. Over 64,000 MT of the caustic were reported as hazardous. This number may have been significantly higher except for the industry's practice to manage spent caustic sent to Merichem as a refinery by-product rather than a spent material. In addition, Merichem actively encourages refineries not to manifest their caustics destined for Merichem.

3.8.2.2 Generation and Management

The §3007 questionnaire responses indicated 917,656 MT of spent caustic were generated in 1992. Residuals were assigned to be "spent caustic from liquid treating" if they were assigned a residual identification code of "spent caustic, which corresponds to residual code 04-A in Section VII.2 of the questionnaire. Caustic from the HF alkylation process, and other residuals on a case-by-case basis, were eliminated from this assignment upon determination that the caustic was not used in a liquid treating operation. In this industry study, spent caustic is the second largest-volume waste being examined. Table 3.8.1 provides a description of the total quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.8.1. Generation Statistics for Spent Caustic from Liquid Treating					
Final Management	# of Streams	# with Unreported Volume	Total Volume (MT)	Average Volume (MT)	90th % Volume (MT)
Storage in a tank	398	36	534,505.3	1,342.98	2,426
Discharge to WWTP; discharge to surface waters; discharge to publically or privately owned treatment works	196	31	246,356.6	1,257	3,989
Disposal in onsite or offsite underground injection well[2]	20	1	11,731.1	586.56	952.5
Disposal onsite surface impoundment	2	0	616.8	308.4	596
Other discharge or disposal offsite	2	0	1,600	800	800
Offsite incineration	1	0	144.6	144.6	144.6
On-site industrial furnace	1	0	791	791	791
Neutralization	24	1	21,631.5	901.31	1,184
Transfer to another petroleum refinery	5	0	284.1	56.82	147
Transfer to a paper mill	6	0	5,599.41	933.24	3,120
Transfer of caustic for reclamation	200	8	450,684	2,253.42	4,649
pH control	10	0	2,211.3	221.13	668.5
Ammonia recovery	2	0	174.8	87.4	165.7
Recycle in FCC wet gas scrubber	2	0	36,209	18,104.5	36,000
Recovery in sulfur plant	2	0	40	20	20
Reuse as desalter water	3	0	904.6	301.53	560
Recovery as pH buffer at WWTP	27	11	21,615.58	800.58	3,173
Reuse onsite in a caustic treater	20	0	13,605.12	680.26	2,425
Onsite caustic regeneration	17	5	96,929.5	5,701.74	30,000
Other misc. recycling, recovery, reclamation	7	0	2,091.8	298.83	900
Total spent caustic[1]	630	82	917,655.8	11,456.6	3,000

[1] Additional miscellaneous non-final management practices were reported, accounting for less than 0.5 percent of the total residual volume. Totals do not add due to possible double counting of interim management steps (i.e., storage, then neutralization, then discharge to WWTP).
[2] Three facilities have onsite injection wells: 2 have Class I wells, 1 did not report in the §3007 survey. Seven facilities send waste to four offsite injection wells: 2 are Class I wells, 2 did not provide data in §3007 survey.

The RCRA §3007 questionnaire showed that the majority of spent caustic is stored in tanks prior to management at the wastewater treatment plant or at Merichem. Merichem uses the cresylic and naphthenic caustics as raw materials (and often purchases these caustics from the refineries) in specialty chemicals manufacturing processes. Their products include a wide range of cresylic and naphthenic acids. Merichem also uses sulfidic caustics as reagents in their processes, but does not typically pay the refineries for these caustics. In addition, Merichem serves as a caustic broker between refineries and paper mills who can use certain sulfidic caustics as a substitute for sodium hydroxide, sodium hydrosulfide, sodium sulfide, or sulfur.

The residual caustic value of the spent caustic is used at some refineries in units where pH control is useful, including desalters, sour water strippers, ammonia control, and wet scrubbers, as well as in the wastewater treatment facilities. A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.8.2.

Given the aqueous nature of the residual and typical management practices, the Agency determined that the risk assessment should model tank storage. Table 3.8.3 characterizes the tanks reported to manage spent caustics in the §3007 questionnaires. Table 3.8.4 provides the volume information used to perform the risk assessment.

The Agency performed a screening analysis to determine the effect of spent caustic on contaminant concentrations in aggressive biological treatment (ABT) sludges at petroleum refining facilities. The analysis was performed by:

- determining the volume of spent caustic discharged to onsite WWTPs,
- determining the average total volume of wastewater discharged to a wastewater treatment facility at a petroleum refinery,
- calculate the proportion of total wastewater volume that is represented by the spent caustic wastestream,
- establish which contaminants occur in wastewater treatment sludges from ABT, establishing which of these contaminants also occur in the spent caustic and focusing the evaluation on these contaminants, and
- apply the dilution factor calculated in Step 3 to the concentration of contaminants in wastewater treatment sludges from ABT to determine the concentration attributed to the spent caustic. (This step assumes that contaminant concentration in the non-spent caustic portion of the wastewater input are equivalent to the concentrations in the spent caustic wastestream.)

The volume of spent caustic discharged to onsite WWTPs was provided in responses to the §3007 survey. The concentration of contaminants detected in the spent caustic were determined through EPA's sampling and analysis. The results of the analysis showed a spent caustic dilution factor of approximately 2.5 percent.

Table 3.8.2. Selection of Risk Assessment Modeling Scenario: Spent Caustic from Liquid Treating	
Waste	**Basis for Consideration in Risk Assessment**
Storage in a tank	Modeled
Discharge to WWTP; discharge to surface waters; discharge to POTW	Not modeled due to coverage of existing sludge listings, the exempt status of effluent discharges, the benzene NESHAPs, the MACT standards for volatile emissions, and the proposed LDR Phase III and IV rulemakings.
Discharge to onsite WWTP	
Discharge to onsite WWTP; ultimate NPDES discharge	
Offsite incineration	Not modeled, Subtitle C incineration
Reuse onsite in a caustic treater	Not modeled, exempt management practice
Transfer of caustic for reclamation	Not modeled, exempt management practice
Discharge to offsite privately-owned wastewater treatment works	Not modeled, covered by existing regulations
Disposal in onsite or offsite underground injection well	Not modeled, covered by existing regulations and LDR Phase III
Disposal onsite surface impoundment	Not modeled, covered by existing regulations and LDR Phase III
Onsite industrial furnace	Not modeled; relatively small volume only reported at one facility out of 630 streams; unlikely to cause emissions concerns
Recycle in FCC wet gas scrubber	Not modeled, exempt management practice
Recovery in sulfur plant	Not modeled, exempt management practice
Reuse as desalter water	Not modeled, exempt management practice
Recovery as pH buffer at WWTP	Not modeled, exempt due to use as an ingredient or reagent substitute (261.2(e))
Transfer to a paper mill	
Transfer to another petroleum refinery	Not modeled, exempt management practice
Onsite caustic regeneration	Not modeled, exempt management practice

The Agency considered whether there was a need to conduct a risk assessment of the wastewater treatment system, but determined that the combinations of the existing F and K sludge listings, the Benzene NESHAPs, and, because of the corrosive characteristic of this waste, the LDR Program's Phase III and Phase IV rulemakings would address any residual risk associated with spent caustics mixed with all other refinery wastewaters (and subsequently significantly diluted to less than 3% of original concentrations). Similarly, the Agency determined that risks associated with underground injection would be adequately addressed by the Phase III rulemakings.

3.8.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.8.5 summarizes the physical properties of the tank sludge as reported in Section VII.A of the §3007 survey.
- Six record samples of spent caustics were collected and analyzed by EPA. These samples represent the three major types of spent caustics generated by the industry and are summarized in Table 3.8.6.

All the samples collected are believed to be representative of spent caustic as generated by the petroleum refining industry. Sulfidic caustics are the most commonly generated (as reported in the survey), followed by cresylic, and, in smallest quantities, naphthenic caustics. The sample profile reflects this distribution. Table 3.8.7 provides a summary of the characterization data collected under this sampling effort.

Table 3.8.3. Spent Caustic Tank Characterization

Parameters	# Reporting "Yes"	# Reporting "No"
Tank Covered?	15	140
Secondary Containment?	108	47
Volume Statistics (MT):	# of RC: 150 # of Unreported values: 5 Mean volume: 381,821 Maximum Volume: 10,722,810 10th Percentile: 8,400 50th Percentile: 42,150 90th Percentile: 860,000	

Table 3.8.4. Management Practices Targeted for Risk Assessment

Spent Caustics from Liquid Treating							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ Unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Storage in Tank	---	398	36	534,505	---	172.15	2,426

Table 3.8.5. Spent Caustic Physical Properties					
Properties	**# of RC**	**# of Unreported Values**	**10th %**	**Mean**	**90th %**
pH	392	316	10	11.92	14
Reactive CN, ppm	70	637	0	24.27	110
Reactive S, ppm	111	596	5	11,546	24,000
Flash Point, °C	105	602	0	245.3	98.9
Oil and Grease, vol%	126	581	0	1.93	5
Total Organic Carbon, vol%	97	610	0	7.6	22
Vapor Pressure, mm Hg	64	643	0.1	13*	50
Viscosity, lb/ft-sec	48	659	0	1.48	10
Specific Gravity	322	386	1.02	1.16	1.3
BTU Content, BTU/lb	62	645	0	747.6	1,000
BOD, mg/L	52	655	0	12,553	25,000
COD, mg/L	54	653	0	47,993	200,000
Aqueous Liquid, %	513	195	90	94.36	100
Organic Liquid, %	370	338	0	4.13	5
Solid, %	369	339	0	2.29	1.5

* Used the 50th percentile because the arithmetic mean was higher than the 90th percentile due to an erroneous data point.

Table 3.8.6. Spent Caustic Record Sampling Locations		
Sample Number	**Facility**	**Description**
R3-LT-01	Exxon, Billings, MT	Tank sampled, concentrated cresylic caustic
R3-LT-02	Exxon, Billings, MT	Tank sampled, concentrated sulfidic caustic
R6-LT-01	Shell, Norco, LA	Naphthenic caustic from treating gas oil and kero
R13-LT-01	Shell, Deer Park, TX	Sulfidic caustic
R12-LT-01	Texaco, Anacortes, WA	Cresylic caustic
R22B-LT-01	Star, Port Arthur, TX	Sulfidic caustic from H_2SO_4 alkylation

3.8.2.4 Source Reduction

> Industry sources indicate that the Agency's investigation of spent caustics for potential listing has influenced some corporations to commit resources to replacing their traditional caustic treating units with hydrotreating and oxidative caustic treating to minimize their potential hazardous waste management burden.

The primary purpose of liquid treating is the removal of sulfur compounds. The industry has several established technological options that generate significantly less residual than liquid treating (but require significant capital expenditure). Hydrotreating technologies remove sulfur compounds and generate residuals (spent catalyst) only upon unit turnaround every 2 to 5 years. Oxidative caustic treating generates much smaller amounts of spent caustic because the sulfur compounds are converted to disulfide oils, which remain in the treated hydrocarbon stream rather than accumulating in the caustic.

Merichem and the paper industry provide recovery opportunities for spent caustics, allowing for the recovery of the cresylic and naphthenic acids and the sulfur content of the spent caustics.

Table 3.8.7. Spent Caustic Characterization

Volatile Organics – Method 8260A µg/L

	CAS No.	R3-LT-01	R3-LT-02	R6-LT-01	R13-LT-01	R12-LT-01	R22B-LT-01	Average Conc	Maximum Conc	Standard Deviation	90% Confidence Interval Upper Limit	Comments
Acetone	67641	15,000	< 500	< 5,000	390,000	6,700	J 50	69,542	390,000	157,085	164,197	
Benzene	71432	J 90	< 500	< 5,000	J 420	2,200	< 50	652	2,200	886	1,261	1
Carbon disulfide	75150	< 500	1,400	< 5,000	< 250	< 500	< 50	540	1,400	516	894	1
Ethylbenzene	100414	J 710	< 500	11,000	540	J 530	< 50	2,272	11,000	4,284	4,853	
n-Propylbenzene	103651	J 660	< 500	< 5,000	J 380	< 500	< 50	215	380	233	723	2
Toluene	108883	J 740	J 200	21,000	920	4,000	< 50	4,465	21,000	8,219	9,437	
1,2,4-Trimethylbenzene	95636	8,500	< 500	51,000	2,200	J 955	< 50	10,534	51,000	20,067	22,626	
1,3,5-Trimethylbenzene	108678	1,600	< 500	20,000	740	< 500	< 50	3,896	20,000	7,905	8,662	
o-Xylene	95476	2,500	< 500	21,000	1,500	J 990	< 50	4,423	21,000	8,165	9,343	
m,p-Xylenes	108383 / 106423	4,000	J 220	49,000	3,000	2,400	< 50	9,778	49,000	19,278	21,394	
Methyl ethyl ketone	78933	6,600	570	11,000	1,400	2,300	< 50	3,653	11,000	4,291	6,239	
Naphthalene	91203	2,900	< 500	29,000	7,600	1,900	< 50	7,025	29,000	11,118	13,724	
4-Methyl-2-pentanone	108101	< 500	< 500	< 5,000	780	< 500	< 50	466	780	262	646	1
Styrene	100425	< 500	< 500	< 5,000	3,300	< 500	< 50	970	3,300	1,317	1,873	1

Semivolatile Organics – Method 8270B µg/L

	CAS No.	R3-LT-01	R3-LT-02	R6-LT-01	R13-LT-01	R12-LT-01	R22B-LT-01	Average Conc	Maximum Conc	Standard Deviation	90% Confidence Interval Upper Limit	Comments
2,4-Dimethylphenol	105679	2,570,000	J 24,000	340,000	E 450,000	E 310,000	1,900	615,983	2,570,000	973,968	1,202,671	
Indene	95136	< 50,000	< 25,000	< 1,250	J 5,800	< 6,250	< 400	2,483	5,800	2,904	5,645	1
Isophorone	78591	< 50,000	< 25,000	< 1,250	16,000	< 6,250	< 400	5,975	16,000	7,164	11,643	1
2-Methylphenol	95487	32,400,000	229,000	99,000	E 150,000	1,900,000	6,600	5,797,433	32,400,000	13,052,152	13,662,327	
3/4-Methylphenol	NA	54,600,000	510,000	170,000	77,000	5,500,000	9,100	10,144,350	54,600,000	21,662,678	23,330,293	
Phenol	108952	92,600,000	1,600,000	24,000	J 5,100	E 22,000,000	8,500	19,372,933	92,600,000	36,903,814	41,610,230	
Benzenethiol	108985	1,130,000	6,070,000	< 2,500	J 4,400	E 1,400,000	< 400	1,434,550	6,070,000	2,355,174	2,853,718	
1-Methylnaphthalene	90120	< 100,000	< 50,000	33,000	< 3,425	J 5,200	< 800	10,606	33,000	15,038	22,923	1
2-Methylnaphthalene	91576	< 50,000	< 25,000	22,000	< 1,713	J 4,700	< 400	7,203	22,000	10,027	15,416	1
Naphthalene	91203	< 50,000	< 25,000	26,000	15,000	J 3,500	< 400	13,960	26,000	11,845	22,101	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R3-LT-01	R3-LT-02	R6-LT-01	R13-LT-01	R12-LT-01	R22B-LT-01	Average Conc	Maximum Conc	Standard Deviation	90% Confidence Interval Upper Limit	Comments
Arsenic	7440382	26.00	5.00	< 0.10	< 0.10	< 0.10	2.40	5.62	26.00	10.17	11.75	
Chromium	7440473	< 0.005	< 0.005	< 0.005	< 0.005	0.015	0.015	0.008	0.015	0.005	0.011	
Cobalt	7440484	< 0.25	< 0.25	< 0.25	< 0.25	23.00	< 0.25	4.04	23.00	9.29	9.64	
Copper	7440508	< 0.013	< 0.013	< 0.013	< 0.013	< 0.013	0.087	0.025	0.087	0.030	0.043	
Iron	7439896	< 0.05	< 0.05	< 0.05	< 0.05	24.00	1.20	4.23	24.00	9.69	10.08	
Lead	7439921	0.27	0.12	< 0.03	< 0.03	< 0.03	< 0.03	0.09	0.27	0.10	0.14	
Manganese	7439965	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	0.016	0.009	0.016	0.003	0.011	
Mercury	7439976	0.270	< 0.005	< 0.005	< 0.005	0.270	< 0.005	0.093	0.270	0.137	0.176	
Potassium	7440097	< 2.50	< 2.50	< 2.50	< 2.50	< 2.50	300.00	52.08	300.00	121.45	125.27	
Selenium	7782492	0.35	0.08	< 0.03	< 0.03	< 0.05	< 0.10	0.11	0.35	0.12	0.18	
Sodium	7440235	110,000	43,000	12,000	38,000	54,000	89,000	59,333	110,000	35,865	80,944	
Thallium	7440280	< 0.05	< 0.05	< 0.05	< 0.05	0.38	< 0.05	0.11	0.38	0.13	0.19	
Zinc	7440666	< 0.01	0.01	0.44	< 0.01	< 0.01	0.08	0.09	0.44	0.17	0.20	

SPENT CAUSTIC from LIQUID TREATING

Miscellaneous Characterization	R3-LT-01	R3-LT-02	R6-LT-01	R13-LT-01	R12-LT-01	R22B-LT-01	Average Conc	Maximum Conc	Standard Deviation	90% Confidence Interval Upper Limit	Comments
Ignitability (oF)	> 210	125	135	> 210	155	> 213	NA	NA	NA		
Corrosivity (pH units)	12	14	13	13	14	13	NA	NA	NA		
Reactivity – Total Releasable H2S (mg/L)	< 25	< 25	< 25	120	770	1,000	328	1,000	439	592	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
E Concentration exceeds the upper calibration standard.
ND Not Detected.
NA Not Applicable.

3.9 H_2S REMOVAL AND SULFUR COMPLEX

3.9.1 Process Description

All crude oil contains sulfur, which must be removed at various points of the refining process. The predominant technique for treating light petroleum gases is (1) amine scrubbing followed by (2) recovery of elemental sulfur in a Claus unit followed by (3) final sulfur removal in a tail gas unit. This dominance is shown in Table 3.9.1, which presents the sulfur complex/removal processes reported in the RCRA §3007 questionnaire.

Table 3.9.1. Sulfur Removal Technologies Reported in RCRA §3007 Questionnaire

Technique	Number of Facilities	Percentage of Facilities[1]
Amine-based sulfur removal	106	86
Claus sulfur recovery[2]	101	82
Other sulfur removal or recovery	16	13
SCOT®-type tail gas unit	50[3]	41
Other tail gas treating unit	19[3]	15

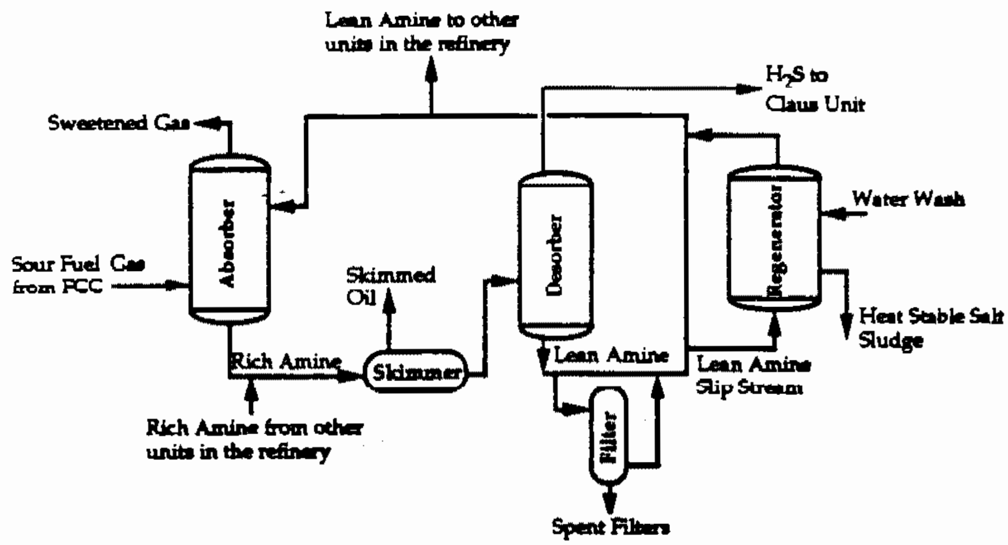
[1] Percentage of the 123 facilities reporting any sulfur removal/complex technique.
[2] Note that more facilities perform sulfur removal than perform sulfur recovery. Some refineries ship their H_2S-containing amine offsite to another nearby refinery.
[3] Only 47 facilities were coded to have SCOT®-like units in the database, but closer examination revealed that 3 additional facilities with "other systems" really had SCOT®-like units.

Caustic or water is often used in conjunction with, or instead of, amine solution to remove sulfur, particularly for liquid petroleum fractions. These processes, however, are generally not considered sulfur removal processes because either (1) the sulfur is not further complexed from these solutions (i.e., is not removed from the solution), or (2) if removed, it occurs in a sour water stripper which is in the domain of the facility's wastewater treatment system. Such processes are considered to be liquid treating with caustic, which is discussed in Section 3.8.

3.9.1.1 Amine Scrubbing

A typical process flow diagram for an amine scrubbing system is shown in Figure 3.9.1. The purpose of the unit is to remove H_2S from refinery fuel gas for economical downstream recovery. Fuel gas from the refinery is fed to a countercurrent absorber with a 25 to 30 percent aqueous solution of amine such as monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA). The H_2S reacts with the amine solution to form a complex, "rich" amine. Typically, a refinery will have several absorbers located throughout the refinery depending on the location of service. These "rich" streams are combined and sent to a common location at the sulfur plant where the H_2S is stripped from the amine in the reverse reaction. The "lean" amine is recycled back to the absorbers.

Figure 3.9.1. Simplified Flow Diagram of the Amine Sulfur Removal Process



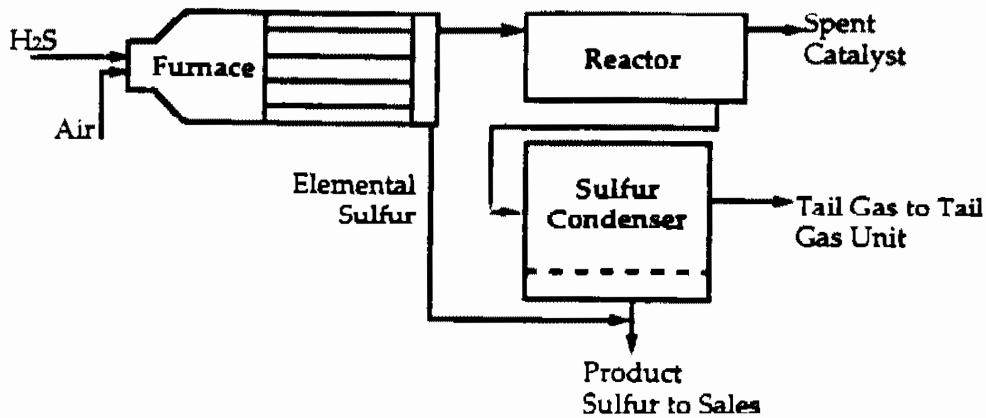
3.9.1.2 Claus Unit

The H_2S from the sulfur removal unit is most often recovered in a Claus system as elemental sulfur. A typical process flow diagram for a Claus unit is shown in Figure 3.9.2. In a Claus unit, the H_2S is partially combusted with air to form a mixture of SO_2 and H_2S. It then passes through a reactor containing activated alumina catalyst to form sulfur by the following endothermic reaction:

$$2\ H_2S + SO_2 \dashrightarrow 3\ S + 2\ H_2O$$

The reaction is typically conducted at atmospheric pressure. The resulting sulfur is condensed to its molten state, drained to a storage pit, and reheated. The typical Claus unit consists of three such reactor/condenser/reheaters to achieve an overall sulfur removal yield of 90 to 95 percent. At this point the tail gas can be (1) combusted and released to the atmosphere, or (2) sent to a tail gas unit to achieve greater sulfur reduction.

Figure 3.9.2. Simplified Flow Diagram of the Claus Sulfur Recovery Process



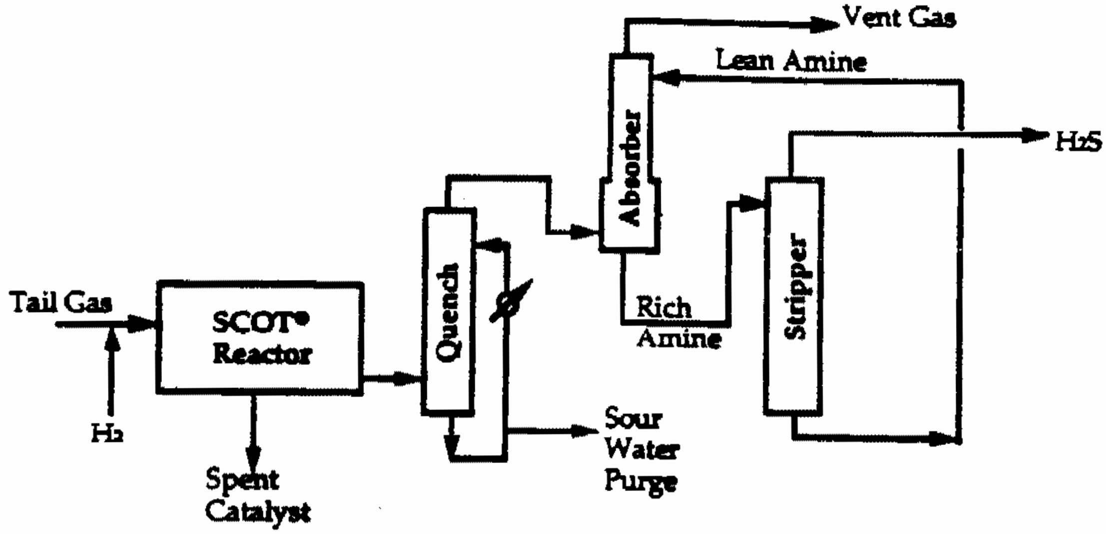
3.9.1.3 SCOT® Tailgas Unit

The most common type of tail gas unit is the Shell Claus Offgas Treating (SCOT®) unit. A typical process flow diagram for a SCOT® unit is shown in Figure 3.9.3. Its purpose is to recover and recycle sulfur, in the form of H_2S, to the Claus unit. Tail gas (containing H_2S and SO_2) is contacted with H_2 and reduced in a hydrotreating reactor to form H_2S and H_2O. The catalyst is typically cobalt/molybdenum on alumina. The gas is then cooled in a water contactor. The water circulates in the column and requires periodic purging due to impurity buildup; filters may be used to control levels of particulates or impurities in the circulating water.

The H_2S containing gas enters an amine absorber which is typically in a system segregated from the other refinery amine systems discussed above. The purpose of this is two-fold: (1) the tail gas frequently uses a different amine than the rest of the plant, such as MDEA or diisopropyl amine (DIPA), and (2) the tail gas is frequently cleaner than the refinery fuel gas (in regard to contaminants) and segregation of the systems reduces maintenance requirements for the SCOT® unit. Amines chosen for use in the tail gas system tend to be more selective for H_2S and are not affected by the high levels of CO_2 in the offgas.

The "rich" amine generated from this step is desorbed in a stripper; the lean amine is recirculated while the liberated H_2S is sent to the Claus unit. Particulate filters are sometimes used to remove contaminants from lean amine.

Figure 3.9.3. Simplified Flow Diagram of the SCOT® Tail Gas Sulfur Removal Process



3.9.1.4 Other Processes

Although the amine/Claus/SCOT® train described above is the dominant system used in the industry, it is not exclusive. Some refineries, mostly small asphalt plants, do not require sulfur removal processes at all, while others use alternative technologies. In order of usage, the alternative processes are as follows:

Sulfur Removal/Recovery Processes

- Sodium hydrosulfide. Fuel gas containing H_2S is contacted with sodium hydroxide in an absorption column. The resulting liquid is product sodium hydrosulfide (NaHS).

- Iron chelate. Fuel gas containing H_2S is contacted with iron chelate catalyst dissolved in solution. H_2S is converted to elemental sulfur, which is recovered.

- Stretford. Similar to iron chelate, except Stretford solution is used instead of iron chelate solution.

- Ammonium thiosulfate. In this process, H_2S is contacted with air to form SO_2. The SO_2 is contacted with ammonia in a series of absorption column to produce ammonium thiosulfate for offsite sale. (Kirk-Othmer, 1983)

- Hyperion. Fuel gas is contacted over a solid catalyst to form elemental sulfur. The sulfur is collected and sold. The catalyst is comprised of iron and naphthoquinonsulfonic acid.

- Sulfatreat. The Sulfatreat material is a black granular solid powder; the H_2S forms a chemical bond with the solid. When the bed reaches capacity, the Sulfatreat solids are removed and replaced with fresh material. The sulfur is not recovered.

- A few facilities report sour water stripping, which is not part of the scope of the survey and is likely to cause severe underestimates of the actual number of sour water strippers in existence.

- Hysulf. This process is under development by Marathon Oil Company. Hydrogen sulfide is contacted with a liquid quinone in an organic solvent such as n-methyl-2-pyrolidone (NMP), forming sulfur. The sulfur is removed and the quinone reacted to its original state, producing hydrogen gas (*The National Environmental Journal*, March/April 1995).

Tail Gas Processes

- Beavon Stretford tail gas. A hydrotreating reactor converts SO_2 in the offgas to H_2S. The H_2S is contacted with Stretford solution (a mixture of vanadium salt, anthraquinone disulfonic acid, sodium carbonate, and sodium hydroxide), where it reacts to form elemental sulfur. The elemental sulfur is recovered and sold.

- Caustic scrubbing. An incinerator converts trace sulfur compounds in the offgas to SO_2. The gas is contacted with caustic which is sent to the wastewater treatment system.

- Polyethylene glycol. Offgas from the Claus unit is contacted with this solution to generate an elemental sulfur product. Unlike the Beavon Stretford process, no hydrogenation reactor is used to convert SO_2 to H_2S. (Kirk-Othmer, 1983)

- Selectox. A hydrogenation reactor converts SO_2 in the offgas to H_2S. A solid catalyst in a fixed bed reactor converts the H_2S to elemental sulfur. The elemental sulfur is recovered and sold. (*Hydrocarbon Processing*, April 1994).

- Sulfite/Bisulfite Tail Gas Treating Unit. Following Claus reactors, an incinerator converts trace sulfur compounds to SO_2. The gas is contacted with sulfite solution in an absorber, where SO_2 reacts with the sulfite to produce a bisulfite solution. The gas is then emitted to the stack. The bisulfite is regenerated and liberated SO_2 is sent to the Claus units for recovery. (Kirk-Othmer, 1983)

3.9.2 Sludge from Sulfur Complex and H_2S Removal Facilities - Residual 15

3.9.2.1 Description

Impurities such as carbon dioxide can irreversibly react with the amine (forming heat stable salts) and interfere with system operation; rust particles can also form in the system. Heat stable salts also can contribute to corrosion by degrading to organic acids, and aiding in the formation of ferrous sulfide. Ferrous sulfide can also contribute to foaming in hydrocarbon/amine separators, resulting in the loss of amine in the hydrocarbon.

For this reason, particulate or heat stable salt removal systems are common on the system's "lean" side. Control methods depend on the type of amine in use, the quality of the fuel gas being treated, economics, etc., and include particulate filters, activated carbon, diatomaceous earth, regeneration (reboiling), and caustic addition. All of these control methods, except caustic addition, generate residuals periodically (weekly to biannually), which are included in the scope of sulfur sludge. Filters and activated carbon require periodic replacement when spent; many facilities backwash the particulates from these filters to the sewer system to prolong the service life of the filters. In a regenerator, the amine/water is boiled off to leave a sludge containing heat stable salts and other corrosion products. Filters and activated carbon can be used for any system, while only low-boiling amine solutions such as MEA are effectively controlled with a reboiler.

Sludge from the sulfur complex includes all sludges, filters, adsorbents, and other media used in a sulfur removal system. Based on the above process descriptions in Section 3.9, the following processes potentially generate sludge:

- Amine-based sulfur removal (106 facilities)
- Stretford-based sulfur removal (2 facilities)
- Other miscellaneous sulfur removal processes (14 facilities)
- SCOT®-like tail gas treatment (50 facilities)
- Beavon-Stretford tail gas treatment (14 facilities)
- Other miscellaneous tail gas treatment processes (5 facilities).

Sludges or wastes from Claus units are generally limited to those generated during turnaround/maintenance activities. Such wastes were generally classified as waste sulfur, a study residual, and were not part of the scope of sulfur sludge. In addition, amine that is discharged from the system is specifically excluded from the scope of "sulfur sludge." Instead, this residual is considered in the scope of off-spec treating solution from sulfur recovery, which is a study residual.

1992 Identification of Sulfur Sludge

D007 (TC Chromium)	2,336 MT
D010 (TC Selenium)	1,216 MT
D003 (Reactive)	1,209 MT

Total identified as hazardous: 2,446 MT (the most common codes are listed; some streams carry multiple codes)

Approximately 2,446 MT of sulfur sludge generated in 1992 were identified as displaying hazardous characteristics. This is approximately 29 percent of the total quantity managed.

3.9.2.2 Generation and Management

As discussed in Section 3.9.1, the amine sulfur removal process is the dominant sulfur removal process for gas streams used in the industry. The next most frequently used process is the Stretford sulfur removal/complex process. Sludges generated from the Stretford process will not be addressed by EPA in its decision-making because it is a small and distinct segment of the industry's sulfur removal capability. The remaining sulfur sludges are generated from the remaining types of processes discussed in Section 3.9.1.

Only sludges from the amine system were considered in the listing determination. Sludges from other processes, including the Stretford process, are specifically excluded because they are generated by far fewer facilities in much smaller quantities than the amine process sludges. Only 2 facilities reported generating sludge from the Stretford process compared to 103 facilities generating sludge from the non-Stretford process.

Based on observations made during engineering site visits, interim management of the sludges sent to wastewater treatment includes contained vacuum trucks or discharge to the facility sewer system. All other interim management is conducted in open or closed drums or dumpsters.

Ninety-four facilities reported generating a total quantity of 8,520 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "sulfur sludge" if they were assigned a residual identification code of "other process sludge" or "spent sorbent" and were generated from a sulfur complex or H_2S removal process. These correspond to residual codes 02-D and 07, respectively, in Section VII.2 of the questionnaire and process code 15 in Section IV-1.C of the questionnaire. Sludges from the Stretford process were segregated on the basis of the generating unit: sludges originating from Stretford systems or Beavon-Stretford tail gas systems (corresponding to process codes 15-B and 15-E, respectively), in Section IV-1.C of the questionnaire were included in this category. Based on the results of the questionnaire, approximately 106 facilities use amine in their refinery sulfur removal system or their tail gas sulfur removal system. The remaining facilities likely do not generate sludges from their amine sulfur removal systems because they can control corrosion and particulates using methods other than ion/solids removal; caustic addition is an example of such a method.

Table 3.9.2 provides a description of the quantity generated, number of streams reported, number of unreported volumes, and average and 90th percentile volumes.

Table 3.9.2. Generation Statistics for Non-Stretford Sulfur Sludge, 1992					
Final Management	# of Streams	# with unreported volume	Total Volume (MT)	Average Volume (MT)	90th % Volume (MT)
Disposal offsite Subtitle D landfill	95	15	4,041	43	70
Discharge to wastewater treatment	33	6	3,442	104	100*
Onsite incineration[2]	3	1	197	66	192
Disposal in onsite Subtitle D landfill	18	0	195	11	53
Disposal offsite in Subtitle C landfill	54	9	149	3	3
Offsite carbon regeneration	15	0	104	7	27
Onsite land treatment	8	1	73	9	50
Offsite land treatment	3	0	34	11	18
Disposal in onsite Subtitle C landfill	13	1	29	2	4
Offsite incineration	9	2	8	1	4
Miscellaneous[1]	15	0	247	16	88
TOTAL	266	35	8,520	32	40

* Estimate

[1] Miscellaneous management includes: recycle to the process, offsite recycling, reuse (not specified if onsite or offsite), regeneration (not specified if onsite or offsite), steam stripping, onsite recovery in coker, transfer to make a fuel, and offsite cleaning of reusable filter disc.

[2] Two facilities: one with a Part B permit and the other uses a trash burner (refractory-lined pit) to burn refuse and non-hazardous process waste.

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the "high potential exposure" disposal practices currently used, which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.9.2 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practices are:

- Offsite Subtitle D landfilling (used for 47 percent of the total quantity of generated sludge). This scenario was chosen because it is used for a significant volume of waste and is expected to be a high potential exposure management method. An onsite monofill scenario was rejected because of the low quantity of residual generated at individual facilities.

- Onsite Subtitle D landfilling (used for 2.3 percent of the total quantity of generated sludge). This scenario was chosen because it is expected to be a high potential exposure management method. An onsite monofill scenario was rejected because of the low quantity of residual generated at individual facilities.

- Onsite land treatment (used for 1 percent of the total quantity of generated sludge). This scenario was chosen because it was demonstrated to be in use and could be used by other facilities.

- Interim onsite storage. This scenario was chosen because all sludges could potentially be stored onsite in open containers prior to further management. The Agency observed during engineering site visits and sampling trips that sludge from sulfur complex operations is generated on a regular basis (e.g., weekly) and the Agency observed facilities that maintain storage areas on the process units for dumpsters used to accumulate filter cartridges. This practice also poses the potential for ongoing air emissions and was modeled in EPA's risk assessment.

The sludges managed in wastewater treatment systems were not chosen for evaluation in the risk assessment because these sludges will settle out in the primary treatment steps and are already listed as hazardous. A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.9.3.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.9.4 provides a summary of the data for the targeted management practices used in the risk assessment for the sulfur sludges.

3.9.2.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.9.5 summarizes the physical properties of the tank sludge as reported in Section VII.A of the §3007 survey.

- Five record samples of actual sludges were collected and analyzed by EPA. These samples represent the various types of sludges generated by the industry and are summarized in Table 3.9.6.

Table 3.9.3. Selection of Risk Assessment Modeling Scenario: Non-Stretford Sulfur Sludge	
Final Management	**Basis for Consideration in Risk Assessment**
Disposal offsite Subtitle D landfill	Modeled
Discharge to wastewater treatment	Not modeled. Sludge would settle out in and be captured by existing hazardous waste listings. Wastewater discharge is exempt. Air pathways controlled by Benzene NESHAPs. Impact on WWTP expected to be minimal due to small volume of waste in relation to the total volume of wastewater typically treated. Sediments would be further controlled by the Phase IV LDR standards when the sediments exhibit any of the characteristics.
Onsite incineration	Not modeled. Majority of waste is burned in Subtitle C permitted unit, no incremental risk to model. Balance of volume is much less than 100 mt.
Disposal in onsite Subtitle D landfill	Modeled
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite carbon regeneration	Not modeled, exempt management
Onsite land treatment	Modeled
Offsite land treatment	Modeled
Disposal in onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite incineration	Not modeled, *de minimis* volume
Miscellaneous[1]	Not modeled, exempt management practices

[1] Miscellaneous management includes: recycle to the process, offsite recycling, reuse (not specified if onsite or offsite), regeneration (not specified if onsite or offsite), steam stripping, onsite recovery in coker, transfer to make a fuel, and offsite cleaning of reusable filter disc.

Table 3.9.4. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Dumpster Storage	–	152	6	4,156	—	0.77	27
Onsite and Offsite Subtitle D Landfill[3,4]	50	113	15	4,236	—	4	69.3
	Onsite Landfill Characteristics						
	Surface Area (acres)				0.46	7.7	36
	Remaining capacity (thousand cu.yd.)				3.7	66.7	6,500
	Percent remaining capacity				0.7	9.5	80
	Total capacity (thousand cu.yd.)				7.3	112.9	8,000
	Number of strata in completed unit				0	1	400
	Depth below grade (ft)				0	7	23
	Height above grade (ft)				0	6	35
	# of Landfills: 16						
	Aquifer Information						
	Depth to Aquifer (ft)				8.5	20	166
	Distance to Private Well (ft)				2,500	6,200	26,400
	Population Using Private Well				1	1.5	2
	Distance to Public Well (ft)				7,000	15,840	58,000
	Population Using Public Well				1,500	1,750	2,000
	# of Aquifers: 15						
	Source: / Public / Private Unreported 12 10 Uppermost 1 2 Lowermost 2 1 Combination – 2						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (2) Not considered a potential source of drinking water (12) Unreported (1)						

Table 3.9.4. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Offsite Land Treatment Unit[2,3]	3	3	0	34	—	10	18.2
Onsite Land Treatment Unit[1,3]	6	8	1	73	—	2.25	50
	Characteristics						
	Surface Area (acres)				4	16	105
	Depth of Incorporation (in)				6	10	12
	Amount Applied (1992 MT)[2]				2	152	10,190
	Methods of Incorporation: Disking 8 Subsurface Injection 1 Bulldozing 1						
	# of Land Treatment Units: 10						
	Aquifer Information						
	Depth to Aquifer (ft)				15	21	97
	Distance to Private Well (ft)				2,000	5,500	25,000
	Population Using Private Well				0	0	1
	Distance to Public Well (ft)				15,000	15,000	15,000
	Population Using Public Well				10,000	10,000	10,000
	# of Aquifers: 9						
	Source: Public / Private Unreported 8 / 4 Uppermost 1 / 2 Lowermost 0 / 1 Combination 0 / 2						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (3) Not considered a potential source of drinking water (5) Unreported (1)						

[1] The number of onsite land treatment units characterized in Table 3.9.4 is greater than indicated in Table 3.9.2 which focuses only on volumes generated in 1992. Table 3.9.4 incorporates data from all onsite land treatment units receiving sludge in any year reported in the §3007 survey.
[2] Volumes represent the average volume of all wastes applied to the land treatment units accepting the non-Stretford sulfur sludge and not just the sulfur sludge alone.
[3] The 50th and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).
[4] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

Table 3.9.5. Sulfur Sludge Physical Properties					
Properties	**# of RC**	**# of Unreported Values**	**10th %**	**Mean**	**90th %**
pH	183	235	4.5	7.9	10
Reactive CN, ppm	102	315	0	29	50
Reactive S, ppm	134	283	0.05	1,347	500
Flash Point, C	110	304	60	84	102
Oil and Grease, vol%	66	349	0	2.1	7.5
Total Organic Carbon, vol%	56	361	0	12.8	63.9
Viscosity, lb/ft-sec	3	414	0	0.02	0.07
Specific Gravity	77	341	0.24	1.5	1.52
BTU Content, BTU/lb	35	382	1,900	8,000	12,700
Aqueous Liquid, %	251	167	0	17.6	75
Organic Liquid, %	222	196	0	3.1	7.5
Solid, %	322	96	25	84.3	100
Particle >60 mm, %	101	317	0	78	100
Particle 1-60 mm, %	86	332	0	29	100
Particle 100 μm-1 mm, %	75	343	0	8.1	30
Particle 10-100 μm, %	73	345	0	7.3	2
Particle <10 μm, %	70	348	0	0.5	0
Mean Particle diameter, microns	20	389	0	480	1,500

Table 3.9.6. Sulfur Sludge Record Sampling Locations		
Sample number	Facility	Description: Amine and sludge type
R1-ME-01	Marathon Indianapolis, IN	MEA, reclaimer bottoms
R5-ME-02	Marathon, Garyville, LA	MDEA, filter cartridges
R6-ME-01	Shell, Norco, LA	DEA, filter cartridges
R14-ME-01	BP, Toledo, OH	DEA, diatomaceous earth
R18-ME-01	Ashland, Canton, OH	MEA, reclaimer bottoms

All of the samples were taken from refinery amine systems and are believed to represent all sludges, sorbents, and filter media generated from amine systems. No samples from the tail gas system units were collected. These residuals are expected to be cleaner because the feeds are cleaner. Therefore, the tail gas treating residuals are expected to exhibit levels of contaminants no higher than those found in the sampled residuals.

Of the sludges characterized, all represent the physical or chemical removal of particulates from a slip stream of amine treating solution. Activated carbon is a frequently used sorption medium which was not sampled; the sampling results of other wastes are expected to represent this residual because similar contaminants are being removed. In addition, none of the sampled residuals were taken from the tail gas treating section.

An effective cross-section of the treating solutions used in refineries was represented in the sampling. The RCRA §3007 Questionnaire did not specifically request information on the type of amine solution used, but based on information supplied by some refineries and from engineering site visits, the solutions MEA and DEA are frequently used to treat refinery fuel gas while MDEA is used less frequently for this purpose. MDEA is frequently used in the SCOT® tail gas unit. Diisopropanol amine (DIPA) is also used for treating.

As discussed in Section 3.9.1, systems other than amine are used to remove sulfur from refinery fuel gas or tail gas. These include, but are not limited to, the Stretford process. These residuals were not represented by the sampling. As stated before, this listing determination focuses on the sludges from the amine treating process because it is the most widely used system.

All six samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. All samples were also analyzed for corrosivity, reactivity, ignitability, and total amines. None of the TCLP extracts of the analyzed samples exhibited levels of constituents in excess of their regulatory levels. One sample exhibited the characteristic of corrosivity, while two samples exhibited levels of releasable H_2S in excess of 1,000 mg/kg. The two MEA reclaimer samples higher levels of iron can be attributed to a higher amount of concentrated corrosion products (rust and scale) in the sludge. A summary of the results is presented in Table 3.9.7. Only constituents detected in at least one sample are shown in this table.

3.9.2.4 Source Reduction

There are many opportunities to reduce the toxicity or volume of this residual. The primary reason sludges are generated is to remove impurities from the amine system to maintain satisfactory operation. Two immediate methods to reducing sludge volume are: (1) using a different amine that is less sensitive to the impurities, and (2) using different methods to control or remove these impurities that would generate less waste.

As an example of the first method, many refineries use methyl diethanolamine (MDEA) instead of monoethanolamine (MEA) at the tail gas unit. MDEA is not as susceptible to the formation of heat stable salts and is amenable to regeneration. Using MDEA greatly reduces the amount of amine sludge generated by the tail gas unit.

Examples to the second method include the following:

- At least two facilities control heat stable salts in their MDEA amine treating system using a proprietary caustic. With heat stable salt generation being controlled, the refineries do not have to use their cloth filters as much and thus can reduce the frequency of generation. Other facilities have mentioned the use of corrosion inhibitors to serve the same purpose.

- Cloth cartridge filters are a common particulate control technique in the amine system. At least two facilities have replaced their cloth or cartridge filters with an etched metal mechanical filter. The new filter requires less maintenance, reduces or eliminates the number of filter elements disposed of, and also conserves the quantity of amine in the system, as amine is no longer lost during the filter change-out procedure.

- At least one facility using treating clay replaced this material with regenerative carbon. The carbon can be regenerated onsite while the clay, presumably, could not be.

Table 3.9.7. Residual Characterization Data for Sulfur Sludge

Volatile Organics – Method 8260A μg/kg

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	6,600	< 25	< 1,250	< 625	J 670	1,834	6,600	2,699	3,665	
Benzene	71432	< 2,500	96	< 1,250	< 625	J 420	258	420	229	757	1, 2
n-Butylbenzene	104518	7,200	< 25	J 700	< 625	< 600	1,630	7,200	3,014	3,696	
Carbon disulfide	75150	< 2,500	150	< 1,250	< 625	< 600	150	150	NA	NA	1
Ethylbenzene	100414	9,600	210	J 1,100	< 625	< 600	2,427	9,600	4,022	5,165	
4-Methyl-2-pentanone	108101	78,000	< 25	< 1,250	< 625	< 600	16,100	78,000	34,606	39,825	
Methylene chloride	75092	< 2,500	< 25	< 1,250	< 625	J 150	88	150	88	260	1, 2
n-Propylbenzene	103651	6,600	< 25	< 1,250	< 625	< 600	1,820	6,600	2,707	3,676	
Toluene	108883	13,000	410	J 510	< 625	< 600	3,029	13,000	5,575	8,851	
1,2,4-Trimethylbenzene	95636	47,000	240	J 1,800	J 600	< 600	10,048	47,000	20,665	24,216	
1,3,5-Trimethylbenzene	108678	16,000	340	J 520	< 625	< 600	3,617	16,000	6,923	8,363	
o-Xylene	95476	16,000	210	< 1,250	< 625	< 600	3,737	16,000	6,665	8,444	
m,p-Xylenes	108383 / 108423	54,000	570	J 1,000	J 790	< 600	11,392	54,000	23,819	27,722	
Naphthalene	91203	34,000	< 25	2,500	J 920	J 240	7,537	34,000	14,825	17,701	

TCLP Volatile Organics – Methods 1311 and 8260A μg/L

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	B 160	< 50	< 50	< 50	B 150	96	160	64	140	
Benzene	71432	< 50	< 50	< 50	< 50	J 26	26	26	NA	NA	1
Ethylbenzene	100414	130	< 50	< 50	< 50	< 50	66	130	36	91	
Methylene chloride	75092	< 50	< 50	< 50	< 50	JB 24	24	24	NA	NA	1
Toluene	108883	500	< 50	< 50	< 50	< 50	140	500	201	276	
1,2,4-Trimethylbenzene	95636	210	< 50	J 23	< 50	< 50	77	210	75	126	
o-Xylene	95476	260	< 50	< 50	< 50	< 50	92	260	94	156	
m,p-Xylene	108383 / 108423	630	< 50	< 50	< 50	< 50	166	630	259	344	
Naphthalene	91203	< 50	< 50	J 49	< 50	JB 14	32	49	25	85	1, 2

Semivolatile Organics – Method 8270B μg/kg

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acenaphthene	83329	J 7,600	< 3,300	< 16,500	< 2,063	< 165	3,332	7,600	3,246	5,990	1
Anthracene	120127	J 5,000	< 3,300	< 16,500	J 980	< 165	2,361	5,000	2,204	4,166	1
Chrysene	218019	< 6,600	< 3,300	< 16,500	J 2,600	< 165	1,363	2,600	1,722	5,130	1, 2
Dibenzofuran	132649	< 6,600	< 3,300	< 16,500	J 1,900	< 165	1,033	1,900	1,227	3,703	1, 2
Fluorene	86737	J 8,700	< 3,300	< 16,500	8,500	< 165	5,166	8,700	4,167	8,579	1
Isophorone	78591	J 6,700	< 3,300	< 16,500	< 2,063	600	3,166	6,700	2,602	5,297	1
2-Methylchrysene	3351324	< 13,200	< 6,600	< 33,000	J 1,400	< 330	665	1,400	757	2,512	1, 2
1-Methylnaphthalene	90120	39,000	37,000	< 33,000	19,000	< 330	25,666	39,000	16,174	36,755	
2-Methylnaphthalene	91576	56,000	87,000	< 16,500	29,000	530	38,206	87,000	34,453	61,626	
Naphthalene	91203	J 13,000	18,000	< 16,500	< 2,063	< 165	9,946	18,000	8,291	15,630	
Phenanthrene	85018	27,000	< 3,300	< 16,500	14,000	560	12,276	27,000	10,665	19,566	
Pyrene	129000	J 6,500	< 3,300	< 16,500	J 4,000	< 165	3,491	6,500	2,608	5,626	1

TCLP Semivolatile Organics – Methods 1311 and 8270B μg/L

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Benzo(a)pyrene	50328	JB 18	< 50	< 50	< 50	< 50	18	18	NA	NA	1
Bis(2-ethylhexyl) phthalate	117817	J 88	< 50	J 96	< 50	< 50	66	96	23	82	
Di-n-butyl phthalate	84742	< 50	JB 16	JB 12	< 50	J 74	40	74	26	58	
1-Methylnaphthalene	90120	J 76	J 32	< 100	J 31	J 18	39	76	25	60	1
2-Methylnaphthalene	91576	J 94	J 68	< 50	J 42	J 17	54	94	29	73	
3/4-Methylphenol (total)	NA	< 50	< 50	< 50	J 66	< 50	53	66	7	58	
Naphthalene	91203	J 93	J 42	< 50	< 50	< 50	57	93	20	71	
Phenanthrene	85018	J 12	< 50	< 50	< 50	< 50	12	12	NA	NA	1
Phenol	108952	< 50	< 50	< 50	170	< 50	74	170	54	111	

SULFUR COMPLEX SLUDGE

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	230.0	340.0	< 20.0	190.0	3,600.0	876.0	3,600.0	1,527.1	1,922.9	
Antimony	7440360	< 6.0	< 6.0	14.0	< 6.0	35.0	13.4	35.0	12.6	22.0	
Arsenic	7440382	33.0	< 1.0	17.0	< 1.0	120.0	34.4	120.0	49.7	68.4	
Cadmium	7440439	1.1	< 0.5	< 0.5	< 0.5	3.3	1.2	3.3	1.2	2.0	
Calcium	7440702	7,700.0	< 500.0	< 500.0	7,500.0	14,000.0	6,040.0	14,000.0	5,692.6	9,942.9	
Chromium	7440473	270.0	18.0	18.0	23.0	900.0	245.8	900.0	381.4	507.3	
Cobalt	7440484	11.0	39.0	< 5.0	< 5.0	24.0	16.8	39.0	14.6	26.8	
Copper	7440508	87.0	94.0	81.0	78.0	150.0	98.0	150.0	29.7	118.4	
Iron	7439896	170,000.0	76,000.0	28,000.0	34,000.0	220,000.0	105,600.0	220,000.0	85,526.8	164,235.2	
Lead	7439921	< 0.3	0.9	< 0.3	0.6	2.7	1.0	2.7	1.0	1.7	
Magnesium	7439954	2,300.0	< 500.0	< 500.0	< 500.0	< 500.0	860.0	2,300.0	805.0	1,411.9	
Manganese	7439965	1,800.0	180.0	270.0	180.0	1,500.0	846.0	1,800.0	871.7	1,443.6	
Molybdenum	7439987	19.0	13.0	< 6.5	< 6.5	64.0	21.8	64.0	24.2	38.4	
Nickel	7440020	60.0	240.0	60.0	19.0	750.0	225.8	750.0	305.3	435.1	
Selenium	7782492	140.0	1.3	9.5	< 0.5	1,200.0	270.3	1,200.0	523.1	628.9	
Sodium	7440235	51,000.0	< 500.0	< 500.0	< 500.0	26,000.0	15,700.0	51,000.0	22,612.5	31,202.6	
Vanadium	7440622	36.0	20.0	< 5.0	< 5.0	< 5.0	14.8	36.0	14.6	24.6	
Zinc	7440666	39.0	10.0	35.0	14.0	88.0	37.2	88.0	31.1	58.5	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Arsenic	7440382	< 0.05	< 0.05	0.49	< 0.05	< 0.05	0.14	0.49	0.20	0.27	
Barium	7440393	< 1.00	< 1.00	2.70	< 1.00	< 1.00	1.34	2.70	0.76	1.86	
Calcium	7440439	51.00	< 25.00	< 25.00	160.00	400.00	132.20	400.00	159.74	241.71	
Chromium	7440473	< 0.05	< 0.05	0.12	< 0.05	0.11	0.08	0.12	0.04	0.10	
Cobalt	7440484	< 0.25	0.91	< 0.25	< 0.25	< 0.25	0.38	0.91	0.30	0.56	
Copper	7440508	< 0.13	< 0.13	0.41	< 0.13	< 0.13	0.18	0.41	0.13	0.27	
Iron	7439896	260.00	130.00	570.00	250.00	280.00	298.00	570.00	163.00	409.75	
Lead	7439921	< 0.02	0.11	1.10	< 0.02	< 0.02	0.25	1.10	0.48	0.58	
Manganese	7439965	36.00	5.10	11.00	2.00	13.00	13.42	36.00	13.37	22.59	
Nickel	7440020	< 0.20	5.90	2.50	< 0.20	1.20	2.00	5.90	2.38	3.63	
Selenium	7782492	< 0.03	< 0.03	< 0.03	< 0.03	0.12	0.04	0.12	0.04	0.07	
Zinc	7440666	< 0.10	1.60	2.40	< 0.10	0.81	1.00	2.40	1.00	1.69	

Miscellaneous Characterization

	CAS No.	R1-ME-01	R5-ME-02	R6-ME-01	R14-ME-01	R18-ME-01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Corrosivity (pH units)		13.3	3.8	9.5	9.9	11.5	NA	NA	NA	NA	
Reactivity – Total ReleasableH2S (mg/kg)		< 25	< 25	< 25	360	8,100	1,707	8,100	3,577	4,159	
Amines – Monoethanolamine (mg/kg)	141435	38,000	NA	< 5	< 5	< 0.5	9,503	38,000	16,998	25,062	
Amines – Etharolamine (mg/kg)	141435	< 500	NA	4,900	< 5	< 0.5	1,351	4,900	2,377	3,298	
Amines – Diethanolamine (mg/kg)	111422	< 500	NA	122,000	14,300	< 0.5	34,200	122,000	58,907	82,445	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations
2 Upper Limit exceeds the maximum concentration.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

3.9.3 Catalyst from Sulfur Complex and H_2S Removal Facilities (Claus Catalyst) Residual 16

3.9.3.1 Description

Claus catalyst is a subset of the larger category of "catalyst from the sulfur complex and H_2S removal facilities." Sulfur catalyst includes all solid sulfur conversion catalyst used in a sulfur removal, recovery or tail gas unit. Liquid catalysts, such as Stretford solution, are not included in this scope but will instead be considered with treating solution from sulfur removal and complex operations, a study residual. Based on the above process descriptions, the following processes use solid catalysts:

- Alumina catalyst from Claus systems (86 facilities)
- Hydrotreating catalyst from SCOT®-like units (50 facilities)
- Hydrotreating catalyst from Beavon-Stretford tail gas treating units (14 facilities).
- Hyperion catalyst (1 facility)
- Other tail gas catalyst (1 facility).

Only alumina catalyst from Claus systems is included in the scope of this listing determination. Hydroprocessing catalyst from SCOT®-like, Beavon-Stretford, and Selectox systems is comprised of a combination of nickel and cobalt or molybdenum on alumina and is discussed in Section 3.3.4 with other hydroprocessing catalysts. The remaining two catalysts are unique to single facilities and because they are used at single facilities, they will not be considered further in this document.

The Claus catalyst requires periodic replacement due to losses in activity. It is generated during turnaround, approximately every 1 to 3 years. Typically, the entire volume of catalyst is removed and placed in containers for off-site management; fresh catalyst is then loaded into the unit.

1992 Identification of Claus Catalyst	
D001 (Ignitable)	68 MT
Managed as haz.	20 MT
D002 (Corrosive)	6 MT
Total identified as hazardous: 94 MT	

Approximately 94 MT of Claus catalyst generated in 1992 were identified as displaying hazardous characteristics. This is approximately 2 percent of the total quantity managed.

3.9.3.2 Generation and Management

Based on observations during engineering site visits and sampling events, interim management of the catalyst is conducted in roll-off bins or closed containers. Sixty-six facilities reported generating a total quantity of 3,819 MT of this residual in 1992, according to the 1992 RCRA §3007 Questionnaire. Residuals were assigned to be "Claus catalyst" if they were assigned a residual identification code of "spent solid catalyst" or "solid catalyst fines" and were generated from a process identified as a Claus unit. These correspond to residual codes 03-A and 03-B, respectively, in Section VII.2 of the questionnaire and process code 15-C in Section IV-1.C of the questionnaire. Catalyst from other units, such as tail gas units and miscellaneous sulfur recovery units discussed in Section 3.9.3.1, are excluded. Quality assurance was conducted by ensuring that all Claus catalysts previously identified in the questionnaire (i.e., in Section V.B) were assigned in Section VII.2. Based on the results of the questionnaire, approximately 101 facilities have Claus reactors. Due to the infrequent generation of this residual, not all facilities with Claus units generated spent catalyst in 1992. However, 1992 is expected to be a typical year in regard to spent catalyst volume and management. Table 3.9.8 provides a description of the quantity generated, number of streams reported, number of zero volumes, and average and 90th percentile volumes.

Table 3.9.8. Generation Statistics for Claus Catalyst, 1992

Final Management	# of Streams	# with unreported volume	Total Volume (MT)	Average Volume (MT)	90th % Volume (MT)
Disposal in offsite Subtitle D landfill	49	1	2,270	46	112
Cement plant	14	0	722	52	170
Disposal in onsite Subtitle D landfill	12	0	407.5	34	60
Disposal offsite in Subtitle C landfill	8	1	256.5	32	107
Offsite metal reclamation	6	0	133	22	59
Disposal in onsite Subtitle C landfill	1	0	12	12	12
Offsite land treatment	1	0	10.3	10.3	10.3
Offsite incineration	1	0	5.8	5.8	5.8
Reuse onsite catalyst support	1	0	1.9	1.9	1.9
TOTAL	93	2	3,819	41	104

Plausible management scenarios were chosen by EPA on which to perform the risk assessment model. The scenarios were chosen based on the numerous "high potential exposure" disposal practices currently used which negated the need for projecting hypothetical "plausible" mismanagement. Given the Agency's past experience with risk assessment modeling, the management practices summarized in Table 3.9.8 were reviewed to identify those practices likely to pose the greatest threats to human health and the environment. The selected management practice is:

- Onsite Subtitle D landfilling (11 percent of the volume of this residual was managed using this method). An onsite monofill scenario was rejected because of the intermittent generation frequency, which is not typical of waste that tends to be monofilled.

- Offsite Subtitle D landfilling (59 percent of the volume of this residual was managed using this method). Risks from disposal in an offsite Subtitle D landfill were assessed because it was the predominant method used in 1992.

A summary of EPA's reasoning in selecting pathways for quantitative risk assessment modeling is presented in Table 3.9.9.

The characterization data for the management units and their underlying aquifers were collected in the §3007 survey. Table 3.9.10 provides a summary of the data for the targeted management practices used in the risk assessment for the Claus catalyst.

Table 3.9.9. Selection of Risk Assessment Scenario: Claus Catalyst	
Final Management	**Basis for Consideration in Risk Assessment**
Disposal in offsite Subtitle D landfill	Modeled
Cement plant	Not modeled, assumed small percentage of feed to cement kiln with very low levels of constituents of concern. Cement would tend to immobilize any trace metals present.
Disposal in onsite Subtitle D landfill	Modeled
Disposal offsite in Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite metal reclamation	Not modeled, see discussion of reclamation practices in Section 3.3.2
Disposal in onsite Subtitle C landfill	Not modeled, already managed as hazardous - no incremental risk to control
Offsite land treatment	Not modeled, very rare practice, small volume unlikely to cause risk
Offsite incineration	Not modeled, very rare practice, small volume unlikely to cause risk
Reuse onsite catalyst support	Not modeled, *de minimis* volumes, exempt management practice

Table 3.9.10. Management Practices Targeted for Risk Assessment							
Parameters	**# of Fac.**	**# of RC**	**# RC w/ unreported Volume**	**Total Volume (MT)**	**10th % Volume (MT)**	**50th % Volume (MT)**	**90th % Volume (MT)**
Onsite and Offsite Subtitle D Landfill[1,2,3]	37	61	1	2,677	---	30	220
	Onsite Landfill Characteristics						
	Surface Area (acres)				0.1	7	36
	Remaining capacity (thousand cu.yd.)				0.7	38	838
	Percent remaining capacity				0.7	9	80
	Total capacity (thousand cu.yd.)				2.0	83.7	840
	Number of strata in completed unit				1	10	208
	Depth below grade (ft)				3	12	25
	Height above grade (ft)				3	12	40
	# of Landfills: 17						
	Aquifer Information						
	Depth to Aquifer (ft)				6	16	166
	Distance to Private Well (ft)				1,000	5,280	26,400
	Population Using Private Well				1	2	10
	Distance to Public Well (ft)				5,000	14,525	58,000
	Population Using Public Well				1,500	2,000	2,000
	# of Aquifers: 17						
	Source: Public / Private Unreported 12 / 11 Uppermost 2 / 3 Lowermost 3 / 1 Combination -- / 2						
	Classification of Uppermost Aquifer: Current or potential source of drinking water (3) Not considered a potential source of drinking water (14)						

[1] The number of onsite landfills characterized in Table 3.9.10 is greater than indicated in Table 3.9.8 which focuses only on volumes generated in 1992. Table 3.9.10 incorporates data from all onsite landfills receiving catalyst in any year reported in the §3007 survey.
[2] The mean and 90th percentile were determined by using a management unit loading method (i.e., more than one waste stream may be disposed of in one management unit causing the 90th percentile number to actually be the sum of 2 or 3 waste volumes).
[3] Models used the same input volumes for both on- and offsite Subtitle D landfill scenarios.

3.9.3.3 Characterization

Two sources of residual characterization were developed during the industry study:

- Table 3.9.11 summarizes the physical properties of the spent Claus catalyst reported in Section VII.A of the §3007 survey.

- Three record samples of actual spent Claus catalysts were collected and analyzed by EPA. These catalysts represent three facilities using the same process and are summarized in Table 3.9.12.

Table 3.9.11. Spent Claus Catalyst Physical Properties

Properties	# of RC	# of Unreported Values	10th %	Mean	90th %
pH	92	112	3.8	5.7	10
Reactive CN, ppm	59	145	0	14.3	10
Reactive S, ppm	70	134	0.01	23.5	100
Flash Point, C	57	147	54.4	95	160
Oil and Grease, vol%	24	177	0	0.3	1.0
Total Organic Carbon, vol%	24	179	0	1.0	2.5
Specific Gravity	73	131	0.75	2.5	3.2
BTU Content, BTU/lb	9	195	0	773	3,000
Aqueous Liquid, %	98	106	0	0.6	2
Organic Liquid, %	88	116	0	1.3	1
Solid, %	160	44	98	99.3	100
Particle >60 mm, %	40	164	0	22	100
Particle 1-60 mm, %	72	132	50	84	100
Particle 100 μm-1 mm, %	57	147	0	6	50
Particle 10-100 μm, %	31	173	0	3	0
Particle <10 μm, %	31	173	0	0.3	0
Mean Particle diameter, microns	17	182	0	4,700	13,000

The collected samples are expected to be representative of the spent Claus unit catalyst as generated. There are essentially no process variations with the Claus process. All units use alumina catalyst and all treat a purified stream of H_2S. Contaminant levels in this catalyst, therefore, are not expected to exhibit significant variation across the industry.

Table 3.9.12. Claus Sulfur Recovery Catalyst Record Sampling Locations		
Sample number	Facility	Description: Catalyst Type
R1-SC-01	Marathon, Indianapolis IN	Alumina
R4-SC-01	Little America, Evansville WY	Alumina
R5-SC-01	Marathon, Garyville LA	Alumina

As discussed in Section 3.9.1, the four sulfur recovery processes in the industry using solid catalyst are the Claus, SCOT®, Selectox, and the Hyperion process. SCOT® catalyst is discussed in Section 3.3.4. The Hyperion and Selectox catalysts are not expected to be represented by this sampling and are not considered in this listing determination.

All three samples were analyzed for total and TCLP levels of volatiles, semivolatiles, and metals. Samples were also analyzed for ignitability. None of the analyzed samples exhibited any hazardous waste characteristic. The high concentration of aluminum can be attributed to the alumina make up of the catalyst. A summary of the results is presented in Table 3.9.13. Only constituents detected in at least one sample are shown in this table.

3.9.3.4 Source Reduction

Like other catalysts, little can be done to reduce the quantity of this generated catalyst since, by design, it must be periodically replaced with fresh catalyst. The greatest pollution prevention opportunity is to prolong the life of the catalyst by improving the quality of the incoming H_2S.

Table 3.9.13. Residual Characterization Data for Spent Claus Unit Catalyst

Volatile Organics – Method 8260A µg/kg

	CAS No.	R1–SC–01	R4–SC–01	R5–SC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	2,500	100	< 20	873	2,500	1,409	2,408	
Acetonitrile	75058	< 625	21	< 20	21	21	1	22	1, 2
Toluene	108883	< 625	< 5	180	93	180	124	352	1, 2
1,2,4–Trimethylbenzene	95636	2,600	< 5	< 20	875	2,600	1,494	2,502	
Methyl ethyl ketone	78933	1,400	38	< 20	486	1,400	792	1,348	
Naphthalene	91203	17,000	< 5	< 20	5,675	17,000	9,808	16,354	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R1–SC–01	R4–SC–01	R5–SC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Acetone	67641	840	< 50	< 50	313	840	456	610	
Acetonitrile	75058	< 50	100	< 50	67	100	29	98	
Methylene chloride	75092	< 50	< 50	130	77	130	46	127	
Naphthalene	91203	160	< 50	< 50	87	160	64	156	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R1–SC–01	R4–SC–01	R5–SC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Di–n–butyl phthalate	84742	< 330	< 165	J 210	235	330	85	328	
2–Methylnaphthalene	91576	J 240	< 165	< 165	190	240	43	237	
Naphthalene	91203	4,200	< 165	< 165	1,510	4,200	2,330	4,047	
1–Methylnaphthalene	90120	J 200	< 330	< 330	200	200	NA	NA	1
Chrysene	218019	J 66	< 165	< 165	66	66	NA	NA	1
Fluoranthene	206440	1,000	480	< 165	548	1,000	422	1,007	2
Phenanthrene	85018	2,800	670	< 165	1,212	2,800	1,399	2,734	
Pyrene	129000	J 500	< 165	< 165	277	500	193	487	

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R1–SC–01	R4–SC–01	R5–SC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Bis (2–ethylhexyl)phthalate	117817	960	J 16	100	359	960	522	928	
Di–n–butyl phthalate	84742	< 50	< 50	JB 12	12	12	NA	NA	1
Naphthalene	91203	J 86	< 50	< 50	62	86	21	85	
Phenol	108952	< 50	< 50	JB 14	14	14	NA	NA	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R1–SC–01	R4–SC–01	R5–SC–01	Average Conc	Maximum Conc	Std Dev	90% Confidence Interval Upper Limit	Comments
Aluminum	7429905	160,000	260,000	130,000	183,000.0	260,000.0	70,000.0	256,221.8	
Arsenic	7440382	13.0	< 5.0	< 10.0	9.3	13.0	4.0	13.7	2
Beryllium	7440417	1.3	< 1.0	< 0.5	0.9	1.3	0.4	1.4	2
Calcium	7440702	< 500.0	22,000.0	< 500.0	7,666.7	22,000.0	12,413.0	21,183.0	
Iron	7439896	130.0	71.0	220.0	140.3	220.0	75.0	222.0	
Selenium	7782492	< 0.5	< 2.5	1.7	1.1	1.7	0.8	2.9	1, 2
Sodium	7440235	2,400.0	< 1,000.0	1,700.0	1,700.0	2,400.0	700.0	2,462.2	2
Zinc	7440666	25.0	51.0	10.0	28.7	51.0	20.7	51.3	2

CLAUS CATALYST from SULFUR COMPLEX

	TCLP Metals - Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L								90% Confidence Interval	
	CAS No.		R1-SC-01	R4-SC-01		R5-SC-01	Average Conc	Maximum Conc	Std Dev	Upper Limit	Comments
Aluminum	7429905		18.00	110.00		48.00	58.67	110.00	46.92	109.76	
Calcium	7440702	<	25.00	640.00	<	25.00	230.00	640.00	355.07	618.63	
Iron	7439896		1.80	5.70		6.50	4.67	6.50	2.51	7.40	2
Manganese	7439965		0.18	0.38		0.28	0.28	0.38	0.10	0.39	2
Zinc	7440666		0.42	0.63	<	0.10	0.38	0.63	0.27	0.87	2

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Upper Limit exceeds the maximum concentration

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

4.0 POPULATION ESTIMATION

The numbers of people potentially exposed to the onsite and offsite management of the residuals of concern are used as input parameters in determining population risk. In addition, the race of people living near refineries is used in presenting environmental justice concerns. The approaches used to establish these input populations are presented in this section. Both the locations of specific residual management locations and the locations of refineries were used with census data to estimate these populations.

4.1 DETERMINING LOCATIONS OF INTEREST

Populations affected by the following residuals and waste management units were required for the population risk assessment:

- offsite landfills managing crude oil tank sludge
- onsite land treatment units managing crude oil tank sludge
- offsite land treatment units managing crude oil tank sludge
- onsite land treatment units managing clarified slurry oil sludge
- offsite land treatment units managing clarified slurry oil sludge
- onsite landfills managing hydrotreating catalyst
- offsite landfills managing hydrotreating catalyst
- onsite landfills managing hydrorefining catalyst
- offsite landfills managing hydrorefining catalyst.

These residuals and waste management practices were chosen on the basis of the risk assessment through both groundwater and above-ground pathways. The procedures used to establish these residuals and disposal scenarios as being of concern are presented in other background documents (e.g., "Assessment of Risks from the Management of Petroleum Refining Wastes: Background Document"). These other background documents also complete the population risk calculations, using the populations presented here as input parameters.

The determination of these locations was performed in a straightforward manner using the Section 3007 survey results. Respondents identified the locations of their onsite or offsite residual management units used in all years that they reported residual generation. To determine the locations of facilities likely to dispose of a specific residual in onsite landfills, those refineries identifying onsite landfilling of the residual in any year were extracted. A similar approach was used to identify onsite land treatment of residuals.

To establish locations of offsite landfill or land treatment facilities for the residuals, a similar approach was used for the crude oil tank sludge and clarified slurry oil sludge. That is, any facility identified by the survey as managing the residual in any year was extracted. For the hydrotreating and hydrorefining catalysts, only those offsite facilities identified as managing the residual in 1992 were extracted. The number of waste management facilities identified for each residual and each scenario is presented in Table 4.1.1.

In the cases of crude oil tank and CSO sludges, individual risks were first calculated on the basis of oily and deoiled sludges, as discussed in Section 3.1 of this document. As a result, populations and population risk were initially calculated using oily and deoiled sludges as well and qualitatively assessed for the combined categories. Table 4.1.2 presents those population estimates required for the initial assessment in terms of oily and deoiled sludges.

4.2 DETERMINING POPULATION AT LOCATIONS OF INTEREST

The locations of the facilities described above were used as inputs to population data systems to quantify the surrounding population. For each location (i.e., each refinery and offsite management unit), one, two, and five mile radii buffer zones were intersected with the Census Bureau block group demographic data. The 1 mile zones were used for the groundwater assessment from landfills. The 1 and 5 mile zones were used for the aboveground (indirect and direct) exposure assessment from land treatment units (the 2 mile zones were not used for any assessment and thus are not presented). Population risk was not required for a groundwater assessment from land treatment units, or an aboveground (indirect and direct) exposure assessment from landfills, because these scenarios were shown to present less than a 10^{-6} individual risk using a high end analysis. For these reasons, five mile populations surrounding landfills were not used and are not presented.

To find locations for onsite units, oil refinery locations (latitude/longitude) were initially obtained from the Federal Emergency Management Agency Master Database as an ARC/INFO point coverage. From these locations, one, two, and five mile radii buffer zones were generated using the ARC/INFO Geographic Information System buffer command.

Offsite management units were located by their zip code centroid by converting the five digit ZIP code to a latitude/longitude by means of a look-up table. This data was stored as an ARC/INFO point coverage. For each offsite management unit, one, two, and five mile radii buffer zones were also generated.

Population data was obtained from the Census Bureau Summary Tape File 1A (STF1A) database. This data was stored as an ARC/INFO point coverage for each state where each point represented the centroid of a Census block group. A block group is a polygon which nominally contains 400 housing units. Demographic statistics such as total population, age, sex, and race structure are compiled for each block group centroid.

Following this procedure, populations for some of the locations could not be obtained due to system errors, missing data, etc. For these locations, assuming a population of zero would underestimate the population. Instead, it was assumed that these facilities would have the same surrounding population as the other locations managing the specific residual. These "scaled" population data were used as the population inputs to the various assessments.

4.3 DETERMINING SUBPOPULATIONS

The populations within one mile of (1) all 171 refineries and (2) all onsite and offsite landfills and land treatment units used to manage the four residuals discussed in this chapter were determined from the same data used above. The data were segregated into the subpopulations of white and non-white. These data are presented in Table 4.3.1. For reference, the national population profile is provided as well. The population data for landfills and land treatment units does not equal the total of all units in Table 4.1.2 because persons in areas with multiple sources were only counted once (i.e., double counting was eliminated).

Table 4.1.1. Population Profile of Waste Management Facilities

Scenario	# of facilities	# of facilities w/ no data	Total population, 1 mile radius	Total population, 1 mile radius, scaled	Total population, 5 mile radius
Crude oil tank sludge, offsite landfill[A]	23	5	45,328	59,093	--
Crude oil tank sludge, onsite land treatment unit	16	0	34,401	34,401	1,869,556
Crude oil tank sludge, offsite land treatment unit	6	0	54,632	54,632	514,449
CSO sludge, onsite land treatment unit	8	0	21,300	21,300	842,698
CSO sludge, offsite land treatment unit	3	0	17,753	17,753	72,871
HTU catalyst, onsite landfill	5	0	1	1	--
HTU catalyst, offsite landfill	12	3	45,379	60,505	--
HRU catalyst, onsite landfill	4	0	1	1	--
HRU catalyst, offsite landfill	4	0	15,758	15,758	--

CSO sludge: clarified slurry oil sludge
HTU catalyst: hydrotreating catalyst
HRU catalyst: hydrorefining catalyst
A. The population surrounding offsite landfills managing crude oil tank sludge was calculated differently than the other residuals. The calculated surrounding population is expected to overestimate the actual surrounding population by no more than 20 percent. The scaled and unscaled populations for oily and deoiled sludges were summed, rather than recalculated to account for single offsite facilities receiving both subsets of this category. Populations surrounding facilities managing oily and deoiled sludges are presented in Table 4.1.2.

Table 4.1.2. Additional Statistics for Crude and CSO Sludges					
Scenario	# of facilities	# of facilities w\ no data	Total population, 1 mile radius	Total population 1 mile radius, scaled	Total population, 5 mile radius
Crude oil tank sludge, deoiled, offsite landfill	15	4	33,016	45,022	--
Crude oil tank sludge, oily, offsite landfill	8	1	12,312	14,071	
Crude oil tank sludge, oily, onsite land treatment unit	9	0	—	—	1,490,341
Crude oil tank sludge, oily, offsite land treatment unit	5	0	—	—	483,169
CSO sludge, oily, onsite land treatment unit	8	0	—	—	842,698
CSO sludge, deoiled, offsite land treatment unit	2	0	—	—	21,690
CSO sludge, oily, offsite land treatment unit	2	0	—	—	67,034

Table 4.3.1. Population Profiles			
	National population profile	Population profile surrounding U.S. petroleum refineries	Population profile surrounding facilities landfilling or land treating proposed listing residuals
Total population	249,402,000	651,757	195,693
White population	209,180,000	408,280	151,955
Percent white	83.9	62.6	77.6
Population of color	40,222,000	243,477	43,738
Percent population of color	16.1	37.4	22.3

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APPENDIX A

1992 RCRA §3007 Survey

Refer to docket for a copy of the RCRA §3007 Survey

APPENDIX B

API Split Sample Comparison

Volatile Organics – Method 8260A µg/kg

	CAS No.	RsB–CS–01	RsB–CS–01B	RsC–CS–01	RsC–CS–01B	Average Conc	Maximum Conc	Minimum Conc	Comments
Acrolein	107028	< 31,250	NR	< 12,500	NR	8,420	24,000	600	1
Benzene	71432	69,000	16,000	220,000	350,000	58,727	220,000	660	
n–Butylbenzene	104518	32,000	19,000	50,000	73,000	29,317	50,000	1,000	
sec–Butylbenzene	135988	21,000	23,000	36,000	63,000	16,528	36,000	270	
tert–Butylbenzene	98066	ND	J 5,400	ND	93,000	NA	NA	NA	2
Ethylbenzene	100414	79,000	66,000	260,000	590,000	67,072	260,000	430	
Isopropylbenzene	98828	32,000	33,000	70,000	110,000	27,420	70,000	420	
p–Isopropyltoluene	99876	19,000	20,000	31,000	59,000	16,342	31,000	250	
Methyl ethyl ketone	78933	6,250	NR	< 12,500	NR	8,892	29,000	600	
n–Propylbenzene	103651	40,000	37,000	110,000	190,000	27,558	110,000	600	
Toluene	108883	200,000	400,000	36,000	460,000	66,307	200,000	340	
1,2,4–Trimethylbenzene	95636	150,000	260,000	330,000	690,000	126,517	330,000	4,100	
1,3,5–Trimethylbenzene	108678	120,000	130,000	160,000	870,000	76,967	160,000	1,700	
o–Xylene	95476	150,000	190,000	320,000	490,000	118,405	320,000	930	
m,p–Xylenes	108383 / 106423	320,000	250,000	830,000	630,000	269,900	830,000	1,400	
Naphthalene	91203	64,000	120,000	210,000	260,000	70,750	210,000	2,400	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	RsB–CS–01	RsB–CS–01B	RsC–CS–01	RsC–CS–01B	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	< 50	NR	270	NR	140	270	50	
Benzene	71432	1,700	1,400	1,800	3,400	679	1,700	32	
Ethylbenzene	100414	240	NR	370	NR	190	370	50	
Toluene	108883	1,900	NR	1,800	NR	703	1,900	50	
1,2,4–Trimethylbenzene	95636	260	NR	160	NR	147	260	24	
1,3,5–Trimethylbenzene	108678	100	NR	J 54	NR	58	100	45	
Methylene chloride	75092	< 50	NR	< 50	NR	70	170	50	
o–Xylene	95476	580	NR	480	NR	273	580	50	
m,p–Xylene	108383 / 106423	1,500	NR	1,300	NR	662	1,500	50	
Naphthalene	91203	150	NR	J 97	NR	116	360	36	

Semivolatile Organics – Method 8270B µg/kg

	CAS No	RsB–CS–01	RsB–CS–01B	RsC–CS–01	RsC–CS–01B	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	< 10,313	NR	13,000	< 33,000	30,621	99,000	413	
Anthracene	120127	< 10,313	NR	< 4,125	J 9,900	27,542	90,000	413	
Benz(a)anthracene	56553	< 10,313	NR	< 4,125	J 36,000	11,470	31,000	413	1
Benzofluoranthene (total)	NA	< 10,313	NR	J 5,900	J 18,000	11,425	29,000	413	1
Benzo(g,h,i)perylene	191242	< 10,313	NR	16,000	J 35,000	10,845	16,000	413	1
Benzo(a)pyrene	50328	J 7,000	J 19,000	J 6,600	J 19,000	12,303	26,000	413	1
Carbazole	86748	< 20,625	NR	< 8,250	< 33,000	48,700	140,000	825	
Chrysene	218019	J 3,000	NR	29,000	63,000	19,193	42,000	413	1
Dibenzofuran	132649	< 10,313	NR	12,000	< 33,000	6,225	12,000	413	
Dibenz(a,h)anthracene	53703	< 10,313	NR	< 4,125	< 33,000	2,058	3,700	413	1
3,3'–Dichlorobenzidine	91941	< 1,875	NR	< 4,750	< 66,000	1,800	1,800	1,800	1
Fluoranthene	206440	< 0,313	NR	J 6,400	J 19,000	25,021	72,000	413	
Fluorene	86737	37,000	J 44,000	32,000	J 55,000	29,800	62,000	1,300	
Indeno(1,2,3–cd)pyrene	193395	< 0,313	NR	J 3,000	< 33,000	14,954	15,000	413	
Phenanthrene	85018	73,000	J 100,000	70,000	200,000	99,133	380,000	7,300	
Pyrene	129000	J 12,000	NR	120,000	190,000	44,235	120,000	413	
1–Methylnaphthalene	90120	240,000	310,000	210,000	430,000	355,417	1,300,000	19,000	
2–Methylnaphthalene	91576	300,000	500,000	450,000	740,000	538,883	2,100,000	5,700	
2–Methylchrysene	3351324	J 6,300	NR	21,000	NR	9,356	21,000	825	1
3/4–Methylphenol	NA	< 0,313	NR	< 4,125	< 33,000	7,670	12,000	413	1
Naphthalene	91203	140,000	230,000	150,000	370,000	129,600	280,000	6,100	

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R6B-CS-01	R6B-CS-01S	R6C-CS-01	R6C-CS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	< 50	NR	< 50	NR	19	19	19	1
Di-n-butylphthalate	84742	< 50	NR	< 50	NR	45	52	15	
Carbazole	86748	< 100	NR	< 100	NR	73	73	73	1
2,4-Dimethylphenol	105679	< 50	NR	< 50	NR	39	39	39	1
Dimethyl phthalate	131113	< 50	NR	< 50	NR	12	12	12	1
Fluorene	86737	< 50	NR	< 50	NR	18	18	18	1
1-Methylnaphthalene	90120	J 33	NR	J 27	NR	142	540	13	
2-Methylnaphthalene	91576	J 38	NR	J 50	NR	180	890	12	
2-Methylphenol	95487	< 50	NR	< 50	J 96	31	31	31	1
3/4-Methylphenol	NA	< 50	NR	< 50	J 29	123	490	50	
Naphthalene	91203	J 85	NR	J 77	NR	126	500	14	
Phenanthrene	85018	< 50	NR	< 50	NR	27	27	27	1
Phenol	108952	< 50	NR	< 50	NR	66	160	47	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R6B-CS-01	R6B-CS-01S	R6C-CS-01	R6C-CS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	2,200.0	1,550	4,600.0	5,170	2,551.7	8,800.0	330.0	
Antimony	7440360	< 6.0	NR	< 6.0	< 6.0	6.5	15.0	6.0	
Arsenic	7440382	6.0	3.3	8.3	8.1	14.6	32.0	5.7	
Barium	7440393	4,400.0	2,700	300.0	320	1,333.3	4,400.0	300.0	
Beryllium	7440417	ND	0.39	ND	< 0.4	NA	NA	NA	2
Cadmium	7440439	1.6	0.66	1.2	< 1.0	1.1	2.0	0.5	
Calcium	7440702	10,000.0	NR	14,000.0	NR	12,033.3	25,000.0	2,300.0	
Chromium	7440473	49.0	38.9	310.0	378	111.6	310.0	2.7	
Cobalt	7440484	15.0	13	360.0	231	72.3	360.0	5.0	
Copper	7440508	130.0	161	170.0	324	292.2	870.0	73.0	
Iron	7439896	18,000.0	NR	25,000.0	NR	111,833.3	300,000.0	15,000.0	
Lead	7439921	210.0	252	44.0	30.9	259.7	870.0	44.0	
Magnesium	7439954	1,200.0	NR	1,400.0	NR	1,466.7	4,200.0	500.0	
Manganese	7439965	110.0	144	150.0	182	661.7	2,200.0	130.0	
Mercury	7439976	0.6	NR	2.5	0.20	1.4	2.5	0.3	
Molybdenum	7439987	< 6.5	NR	880.0	618	158.5	880.0	6.5	
Nickel	7440020	44.0	79.2	380.0	284	112.7	380.0	15.0	
Sodium	7440235	2,800.0	NR	6,300.0	NR	2,115.7	5,300.0	600.0	
Thallium	7440280	ND	1.4	ND	< 2.0	NA	NA	NA	2
Vanadium	7440622	10.0	6.2	1,400.0	1,060	241.7	1,400.0	5.0	
Zinc	7440666	870.0	579	640.0	731	756.7	1,200.0	360.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6B-CS-01	R6B-CS-01S	R6C-CS-01	R6C-CS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Barium	7440393	< 1.00	0.93	2.40	3.0	2.17	3.00	1.00	
Calcium	7440702	< 25.00	NR	550.00	NR	208.33	550.00	25.00	
Iron	7439896	1.40	NR	110.00	NR	174.97	800.00	1.40	
Manganese	7439965	0.15	NR	1.30	NR	2.17	7.80	0.15	
Zinc	7440666	0.26	NR	0.21	NR	0.31	0.83	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR *Not Reported, or concentration below the method detection limit.*

UNLEADED GASOLINE TANK SLUDGE

Volatile Organics – Method 8260A µg/kg

	CAS No.	R6B–US–01	R6B–US–01S	R8A–US–01	R8A–US–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432	43,000	17,000	110,000	77,000	61,900	110,000	2,700	
n–Butylbenzene	104518	73,000	NR	210,000	140,000	120,000	210,000	73,000	
sec–Butylbenzene	135988	J 12,000	10,000	< 25,000	< 25,000	14,933	25,000	7,600	
tert–Butylbenzene	98066	ND	NR	ND	74,000	NA	NA	NA	2
Ethylbenzene	100414	290,000	340,000	450,000	350,000	266,000	450,000	58,000	
Isopropylbenzene	98828	27,000	19,000	< 25,000	< 25,000	21,000	27,000	11,000	
p–Isopropyltoluene	99876	ND	18,000	ND	81,000	NA	NA	NA	2
n–Propylbenzene	103651	130,000	98,000	230,000	230,000	132,667	230,000	38,000	
Toluene	108883	890,000	240,000	740,000	1,200,000	505,000	740,000	85,000	
1,2,4–Trimethylbenzene	95636	740,000	610,000	1,300,000	E 2,200,000	813,333	1,300,000	400,000	
1,3,5–Trimethylbenzene	108678	230,000	680,000	460,000	610,000	283,333	460,000	160,000	
o–Xylene	95476	440,000	340,000	540,000	550,000	140,000	640,000	240,000	
m,p–Xylenes	108383 / 106423	1,400,000	920,000	1,300,000	670,000	1,103,333	1,400,000	610,000	
Naphthalene	91203	170,000	27,000	350,000	520,000	179,667	350,000	19,000	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	F6B–US–01	R6B–US–01S	R8A–US–01	R8A–US–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Methylene chloride	75092	< 50	NR	150	NR	63	150	50	
Benzene	71432	600	440	1,600	3,800	752	1,600	55	
Methyl ethyl ketone	78933	ND	980	ND	< 100	NA	NA	NA	2
Ethylbenzene	100414	1,100	NR	1,500	NR	983	1,500	290	
n–Propylbenzene	103651	240	NR	270	NR	190	270	60	
Toluene	108883	1,700	NR	8,000	NR	3,550	8,000	950	
1,2,4–Trimethylbenzene	95636	1,500	NR	2,300	NR	1,667	2,300	1,200	
1,3,5–Trimethylbenzene	108678	560	NR	700	NR	520	700	300	
o–Xylene	95476	1,900	NR	3,000	NR	2,100	3,000	1,400	
m,p–Xylene	108383 / 106423	3,200	NR	8,100	NR	4,000	8,100	2,700	
Naphthalene	91203	920	NR	1,000	NR	853	1,000	640	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	F6B–US–01	R6B–US–01S	R8A–US–01	R8A–US–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	J 780	NR	J 900	< 33,000	643	900	250	
Anthracene	120127	J 760	NR	< 1,650	< 33,000	463	760	165	1
Bis(2–ethylhexyl)phthalate	117817	7,600	J 6,000	< 1,650	< 33,000	3,138	7,600	165	
Indene	95136	42,000	32,000	72,000	< 33,000	38,297	72,000	390	
Fluorene	86737	J 1,400	NR	J 1,800	< 33,000	1,122	1,800	165	
Phenanthrene	85018	J 2,400	J 2,000	J 1,400	< 33,000	1,322	2,400	165	
Pyrene	129000	J 930	NR	< 1,650	< 33,000	548	930	165	1
1–Methylnaphthalene	90120	140,000	110,000	150,000	140,000	102,333	150,000	17,000	
2–Methylnaphthalene	91576	260,000	260,000	310,000	380,000	222,567	310,000	98,000	
Naphthalene	91203	190,000	180,000	400,000	500,000	213,000	400,000	49,000	

UNLEADED GASOLINE TANK SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R6B-US-01	R6B-US-01S	R8A-US-01	R8A-US-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	370	NR	< 50	NR	157	370	50	
2,4-Dimethylphenol	105679	120	NR	130	NR	95	130	35	
2-Methylphenol	95487	150	120	160	150	120	160	90	
3/4-Methylphenol	NA	160	140	180	190	130	180	50	
Indene	95136	390	NR	J 100	NR	172	390	28	
1-Methylnaphthalene	90120	190	NR	J 100	NR	167	210	100	
2-Methylnaphthalene	91576	320	NR	200	NR	307	400	200	
Naphthalene	91203	780	NR	830	NR	750	830	640	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R6B-US-01	R6B-US-01S	R8A-US-01	R8A-US-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	380.0	489	< 100.0	340	827	2,000	100.0	
Antimony	7440360	18.0	NR	< 30.0	< 30.6	37.7	65.0	18.0	
Arsenic	7440382	35.0	159	240.0	107	97.3	240.0	17.0	
Cadmium	7440439	1.4	NR	< 2.5	< 2.6	3.1	5.5	1.4	
Chromium	7440473	93.0	B 71.9	99.0	B 154	110.7	140.0	93.0	
Cobalt	7440484	20.0	22.2	< 25.0	35.2	33.3	65.0	20.0	
Copper	7440508	250.0	B 298	220.0	B 200	226.7	250.0	210.0	
Iron	7439896	340,000.0	NR	350,000.0	NR	413,333	550,000	340,000	
Lead	7439921	280.0	550	280.0	226	273.3	280.0	260.0	
Manganese	7439965	1,300.0	1,880	1,500.0	1,390	1,733.3	2,400.0	1,300.0	
Mercury	7439976	0.10	0.4	0.27	0.21	0.18	0.27	0.1	
Molybdenum	7439987	14.0	27.3	< 32.5	< 10	38.8	70.0	14.0	
Nickel	7440020	550.0	516	< 20.0	< 20.0	1,823.3	4,900.0	20.0	
Vanadium	7440622	< 50.0	12.2	73.0	17.5	59.3	73.0	50.0	
Zinc	7440666	190.0	297	3,380.0	1,430	1,187.0	3,300.0	71.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R6B-US-01	R6B-US-01S	R8A-US-01	R8A-US-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Barium	7440393	ND	0.87	ND	0.48	NA	NA	NA	2
Chromium	7440473	ND	NR	ND	0.031	NA	NA	NA	2
Iron	7439896	550.0	NR	210.0	NR	254.6	550.0	3.90	
Lead	7439921	0.03	0.056	0.07	0.077	0.04	0.07	0.02	
Manganese	7439965	7.30	NR	2.40	NR	3.80	7.30	1.70	
Nickel	7440020	8.70	NR	< 0.20	NR	28.97	80.00	0.20	
Zinc	7440666	1.80	NR	15.00	NR	5.76	15.00	0.65	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

Volatile Organics – Method 8260A µg/kg

	CAS No.		R4-SO-01		R4-SO-018		R9-SO-01		R9-SO-018	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	<	1,250		NR	<	625		NR	1,869	3,400	625	
Benzene	71432	<	1,250	J	360	J	1,200		2,400	1,200	1,200	1,200	1
n-Butylbenzene	104518	<	1,250		790		1,800		1,800	10,513	22,000	1,250	
sec-Butylbenzene	135988	<	1,250		NR	<	625		NR	1,669	3,000	625	
Ethylbenzene	100414	<	1,250		2,300		4,300		8,500	9,386	20,500	1,250	
Isopropylbenzene	98828	<	1,250	J	110	<	625	J	420	1,769	2,900	625	
p-Isopropyltoluene	99876	<	1,250		740	<	625	J	450	1,769	2,800	625	
Naphthalene	91203		2,900		12,000		11,000		15,000	43,225	140,000	2,900	
n-Propylbenzene	103651	<	1,250		1,100		2,700		8,800	1,925	2,700	1,250	
Toluene	108883		3,900		4,600		8,700		15,000	10,650	17,000	3,900	
1,2,4-Trimethylbenzene	95636		11,000		13,000		20,000	E	27,000	49,000	140,000	11,000	
1,3,5-Trimethylbenzene	108678		2,600		3,200		5,500		7,600	21,300	42,000	2,600	
o-Xylene	95476		3,000		4,700		7,500		15,000	19,375	40,000	3,000	
m,p-Xylenes	108383 / 106423		11,000		5,700		19,000		16,000	49,750	100,000	11,000	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R4-SO-01		R4-SO-018		R9-SO-01		R9-SO-018	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	<	50		NR	<	50		NR	128	360	50	
Benzene	71432	<	50	J	18	J	84		75	59	84	50	
Methylene chloride	75092	<	50		NR	<	50		NR	70	90	50	
Naphthalene	91203	<	50		NR	<	50		NR	110	200	50	
Toluene	108883	B	260		NR		180		NR	175	260	80	
1,2,4-Trimethylbenzene	95636	<	50		NR	<	50		NR	78	110	50	
o-Xylene	95476	B	110		NR	<	50		NR	83	110	50	
m,p-Xylene	108383 / 106423	B	250		NR		100		NR	190	250	100	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R4-SO-01		R4-SO-018		R9-SO-01		R9-SO-018	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	<	61,875	<	165,000		46,000	J	53,000	80,219	160,000	46,000	
Anthracene	120127	<	61,875	<	165,000		77,000	J	90,000	84,219	88,000	32,000	
Benz(a)anthracene	56553		360,000	<	165,000		390,000		730,000	202,969	360,000	20,625	
Benzofluoranthene (total)	NA	J	110,000	J	130,000		110,000	J	210,000	76,750	110,000	27,000	
Benzo(g,h,i)perylene	191242	J	90,000	J	86,000		100,000	J	150,000	69,000	100,000	23,000	
Benzo(a)pyrene	50328		230,000	J	210,000		170,000	J	340,000	132,000	230,000	52,000	
Carbazole	86748	<	123,750	<	165,000		87,000	J	89,000	65,063	87,000	41,250	1
Chrysene	218019		700,000	<	165,000		860,000		1,800,000	487,500	860,000	170,000	
Dibenz(a,h)anthracene	53703	<	61,875	J	53,000		49,000		NR	36,958	49,000	20,625	1
Dibenzofuran	132649	<	61,875		NR		21,000		NR	29,867	37,000	21,000	1
7,12-Dimethylbenz(a)anthracene	57976	<	61,875		NR		1,200,000		NR	330,938	1,200,000	20,625	
Fluoranthene	206440	J	43,000	J	40,000		130,000		NR	62,500	130,000	26,000	
Fluorene	86737	<	61,875	<	165,000		110,000	J	130,000	111,469	200,000	61,875	
Indeno(1,2,3-cd)pyrene	193395	<	61,875		NR		26,000		NR	23,313	26,000	20,625	1
3-Methylcholanthrene	56495	<	61,875		NR	<	20,625		NR	23,813	27,000	20,625	1
2-Methylchrysene	3351324		660,000		NR		460,000		NR	362,500	660,000	180,000	
1-Methylnaphthalene	90120	J	140,000	J	140,000		290,000	J	200,000	800,000	2,200,000	140,000	
2-Methylnaphthalene	91576		190,000	J	200,000		420,000		400,000	1,292,500	3,600,000	190,000	
2-Methylphenol	95487	J	32,000		NR	<	20,625		NR	24,417	32,000	20,625	1
3/4-Methylphenol (total)	NA	J	41,000		NR	<	20,625		NR	27,417	41,000	20,625	1
Naphthalene	91203	J	82,000	J	63,000		68,000	J	100,000	172,500	360,000	62,000	
Phenanthrene	85018		200,000	J	180,000		1,000,000		1,800,000	550,000	1,000,000	200,000	
Phenol	108952	J	93,000	<	165,000	J	7,500	J	61,000	40,619	93,000	7,000	
Pyrene	129000		480,000	J	300,000		610,000		1,100,000	482,500	610,000	210,000	

CSO SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R4-SO-01	R4-SO-01S	R9-SO-01	R9-SO-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	< 50	NR	JB 21	NR	21	21	21	1
Di-n-butyl phthalate	84742	< 50	NR	J 39	NR	39	39	39	1
2,4-Dimethylphenol	105879	< 50	NR	< 50	NR	60	91	50	
1-Methylnaphthalene	90120	< 50	NR	JB 17	NR	64	140	17	
2-Methylnaphthalene	91576	J 27	NR	J 22	NR	68	210	14	
2-Methylphenol	95487	< 50	< 26	< 50	J 11	59	86	50	
3,4-Methylphenol (total)	NA	< 50	< 26	< 50	J 16	52	76	32	
Naphthalene	91203	J 32	NR	J 23	NR	89	176	23	
Phenanthrene	85018	< 50	NR	J 12	NR	12	12	12	1
Phenol	108952	< 50	NR	< 50	NR	76	120	50	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R4-SO-01	R4-SO-01S	R9-SO-01	R9-SO-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	59,000	22,400	22,000	20,100	37,250	59,000	22,000	
Antimony	7440360	< 6.0	< 3	940.0	529	239.5	940.0	6.0	
Arsenic	7440382	< 5.0	1.6	4.7	2.0	2.9	4.7	1.0	1
Barium	7440393	150.0	93.7	48.0	42.7	105.8	170.0	48.0	
Beryllium	7440417	1.2	< 0.1	< 0.5	0.39	0.7	1.2	0.5	
Cadmium	7440439	ND	< 0.25	ND	0.62	NA	NA	NA	3
Calcium	7440702	1,100.0	NR	< 500.0	NR	25,525.0	100,000.0	500.0	
Chromium	7440473	25.0	21.1	6.4	7.6	23.4	34.0	6.4	
Cobalt	7440484	ND	4	ND	3.1	NA	NA	NA	3
Copper	7440508	20.0	16.1	7.8	B 6.7	23.5	53.0	7.8	
Iron	7439896	5,000.0	NR	2,400.0	NR	6,175.0	11,000.0	2,400.0	
Lead	7439921	23.0	16.6	17.0	7.5	26.0	47.0	17.0	
Magnesium	7439954	< 500.0	NR	< 500.0	NR	2,375.0	6,000.0	500.0	
Manganese	7439965	30.0	20.6	15.0	12.3	76.8	240.0	15.0	
Mercury	7439976	0.11	NR	< 0.05	NR	0.07	0.11	0.1	
Molybdenum	7439987	< 6.5	3.4	< 6.6	4.6	44.9	160.0	6.5	
Nickel	7440020	300.0	196	120.0	120	160.5	300.0	62.0	
Potassium	7440097	< 500.0	NR	< 600.0	NR	3,125.0	11,000.0	500.0	
Selenium	7782492	< 0.5	NR	< 0.5	NR	1.7	5.1	0.5	
Sodium	7440235	5,200.0	NR	1,700.0	NR	2,625.0	5,200.0	1,600.0	
Thallium	7440280	< 1.0	NR	< 1.0	NR	1.4	2.6	1.0	
Vanadium	7440622	430.0	324	260.0	277	277.6	430.0	91.0	
Zinc	7440666	100.0	66.9	24.0	23.3	55.0	100.0	24.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R4-SO-01	R4-SO-01S	R9-SO-01	R9-SO-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	< 1.00	NR	< 1.00	NR	2.93	7.00	1.00	
Antimony	7440360	ND	NR	ND	0.38	NA	NA	NA	2
Barium	7440393	ND	0.026	ND	0.84	NA	NA	NA	2
Calcium	7440702	< 25.00	NR	< 25.00	NR	1,143.75	4,500.00	25.00	
Iron	7439896	< 0.50	NR	< 0.50	NR	1.00	2.00	0.50	
Magnesium	7439954	< 25.00	NR	< 25.00	NR	78.75	240.00	25.00	
Manganese	7439965	< 0.08	NR	< 0.08	NR	1.21	4.40	0.08	
Nickel	7440020	< 0.20	NR	< 0.20	NR	0.28	0.52	0.20	
Potassium	7440097	< 25.00	NR	< 25.00	NR	108.75	880.00	25.00	
Zinc	7440666	0.26	NR	< 0.10	NR	0.21	0.37	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with AR data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.

FCC EQUILIBRIUM CATALYST

Volatile Organics – Method 8260A μg/kg

	CAS No.		R4-FC-01		R4-FC-01S		R6-FC-01		R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Chloroethane	75003		ND		ND		ND	J	520	NA	NA	NA	2
Acetone	67641		ND		2,400		ND		ND	NA	NA	NA	2
Benzene	71432		ND		660		ND		ND	NA	NA	NA	2
n-Butylbenzene	104518		ND	J	820		ND		ND	NA	NA	NA	2
Ethylbenzene	100414		6,400		4,600	<	570		ND	3,485	6,400	570	
Isopropylbenzene	98828		ND	J	350		ND		ND	NA	NA	NA	2
n-Propylbenzene	103651		2,200		1,200	<	570		ND	1,385	2,200	570	
Toluene	108883		17,000		14,000	<	570		ND	8,785	17,000	570	
1,2,4-Trimethylbenzene	95636		13,000		9,100		1,300		ND	7,150	13,000	1300	
1,3,5-Trimethylbenzene	108678		5,100		3,500	<	570		ND	2,835	5,100	570	
o-Xylene	95476		11,000		8,100	<	570		ND	5,785	11,000	570	
m,p-Xylenes	108383 / 106423		35,000		13,000	<	570		ND	17,785	35,000	570	
Methyl ethyl ketone	78933		1,400		NR	<	570		NR	985	1,400	570	
Methylene chloride	75092		ND	BJ	390		ND	J	140	NA	NA	NA	2
Naphthalene	91203	<	625		1,200		3,000		ND	1,813	3,000	625	

TCLP Volatile Organics – Methods 1311 and 8260A μg/L

	CAS No.		R4-FC-01		R4-FC-01S		R6-FC-01		R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641		100		NR	<	50		NR	75	100	50	
Toluene	108883	B	160		NR	<	50		NR	105	160	50	
m,p-Xylenes	108383 / 106423	B	150		NR	<	50		NR	100	150	50	
Methyl ethyl ketone	78933		150		NR	<	50		NR	100	150	50	

Semivolatile Organics – Method 8270B μg/kg

	CAS No.		R4-FC-01		R4-FC-01S		R6-FC-01		R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benz(a)anthracene	56553		ND		ND		ND	J	38	NA	NA	NA	2
Chrysene	218019		ND		ND		ND	J	190	NA	NA	NA	2
Dibenz(a,h)anthracene	53703		ND		ND		ND	J	42	NA	NA	NA	2
Dibenzofuran	132649		ND		ND		ND	J	95	NA	NA	NA	2
Fluoranthene	206440		ND		ND		ND	J	37	NA	NA	NA	2
Fluorene	86737		ND		ND		ND	J	190	NA	NA	NA	2
1-Methylnaphthalene	90120	J	510		460	<	165		620	568	510	165	
2-Methylnaphthalene	91576		870		810	<	165		600	923	870	165	
Naphthalene	91203		670		620	<	165		1,300	728	670	165	
1,4-Naphthoquinone	130154		ND		ND		ND	J	130	NA	NA	NA	2
Phenanthrene	85018		ND		ND		ND		5,300	NA	NA	NA	2
Di-n-butyl phthalate	84742	<	165		NR		1,000	J	33	583	1,000	165	

TCLP Semivolatile Organics – Methods 1311 and 8270B μg/L

	CAS No.		R4-FC-01		R4-FC-01S		R6-FC-01		R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis (2-ethylhexyl)phthalate	117817	JB	23		NR	J	15		NR	19	23	15	

FCC EQUILIBRIUM CATALYST

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R4-FC-01	R4-FC-01S	R6-FC-01	R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	89,000.0	49,000	31,000.0	19,200	60,000.0	89,000.0	31,000.0	
Antimony	7440360	ND	ND	ND	50.1	NA	NA	NA	2
Arsenic	7440382	< 1.0	ND	2.5	ND	1.8	2.5	1.0	
Barium	7440393	190.0	122	< 20.0	21.6	105.0	190.0	20.0	
Beryllium	7440417	2.7	ND	1.7	1.1	2.2	2.7	1.7	
Cadmium	7440439	ND	ND	ND	3	NA	NA	NA	2
Calcium	7440702	1,700.0	NR	< 500.0	NR	1,100.0	1,700.0	500.0	
Chromium	7440473	17.0	10.2	4.0	5.3	10.5	17.0	4.0	
Cobalt	7440484	< 5.0	4.7	18.0	23.2	11.5	18.0	5.0	
Copper	7440508	19.0	10.4	13.0	14	16.0	19.0	13.0	
Iron	7439896	4,800.0	NR	1,000.0	NR	2,900.0	4,800.0	1,000.0	
Lead	7439921	42.0	33.7	11.0	11.1	26.5	42.0	11.0	
Manganese	7439965	32.0	20.3	< 1.5	4.9	16.8	32.0	1.5	
Molybdenum	7439987	ND	4.3	ND	9.6	NA	NA	NA	2
Nickel	7440020	330.0	187	91.0	117	210.5	330.0	91.0	
Sodium	7440235	9,800.0	NR	1,900.0	NR	5,850.0	9,800.0	1,900.0	
Thallium	7440280	ND	0.58	ND	NR	NA	NA	NA	2
Vanadium	7440622	1,200.0	823	720.0	978	960.0	1,200.0	720.0	
Zinc	7440666	68.0	36	9.3	11.9	38.7	68.0	9.3	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R4-FC-01	R4-FC-01S	R6-FC-01	R6-FC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Antimony	7440360	< 0.30	NR	2.00	2.1	1.15	2.00	0.3	
Barium	7440393	ND	0.17	ND	0.25	NA	NA	NA	2
Chromium	7440473	ND	0.016	ND	ND	NA	NA	NA	2
Iron	7439896	< 0.50	NR	1.30	NR	0.90	1.30	0.5	
Nickel	7440020	< 0.20	NR	1.10	NR	0.65	1.10	0.2	
Vanadium	7440622	9.50	NR	0.85	NR	5.18	9.50	0.9	
Zinc	7440666	0.25	NR	< 0.10	NR	0.18	0.25	0.1	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

FCC EQUILIBRIUM CATALYST FINES

Volatile Organics – Method 8260A µg/kg

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	ND	ND	ND	ND	ND	40	ND	B 52	NA	NA	NA	2
Benzene	71432	ND	J 180	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
Carbon disulfide	75150	ND	ND	ND	ND	ND	J 1.6	ND	ND	NA	NA	NA	2
Ethylbenzene	100414	ND	600	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
Methylene chloride	75092	ND	J 170	ND	BJ 350	ND	ND	ND	ND	NA	NA	NA	2
n-Propylbenzene	103651	ND	J 150	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
Toluene	108883	1,400	940	< 5	ND	< 5	ND	< 5	ND	354	1,400	5	
1,2,4-Trimethylbenzene	95636	ND	J 250	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
1,3,5-Trimethylbenzene	108678	ND	J 110	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
o-Xylene	95476	ND	J 490	ND	ND	ND	ND	ND	ND	NA	NA	NA	2
m,p-Xylenes	108383 / 106423	1,500	560	< 5	ND	< 5	ND	< 5	ND	379	1,500	5	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Methylene chloride	75092	< 50	NR	< 50	NR	B 140	NR	< 50	NR	73	140	50	
Toluene	108883	< 50	NR	B 250	NR	< 50	NR	< 50	NR	100	250	50	
o-Xylene	95476	< 50	NR	B 87	NR	< 50	NR	< 50	NR	59	87	50	
m,p-Xylenes	108383 / 106423	< 50	NR	B 210	NR	< 50	NR	< 50	NR	90	210	50	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	J 250	ND	< 165	ND	< 165	560	J 110	J 34	173	250	110	
2-Methylnaphthalene	91576	< 165	ND	< 165	ND	J 81	J 91	J 170	J 250	126	170	81	1
1-Methylnaphthalene	90120	< 330	ND	< 330	ND	J 85	J 87	J 150	J 190	118	150	85	1
Benz(a)anthracene	56553	< 165	ND	< 165	ND	J 76	J 69	< 165	ND	76	76	76	1
Benzo(a)pyrene	50328	ND	ND	ND	ND	ND	J 59	ND	ND	NA	NA	NA	2
Chrysene	218019	< 165	ND	< 165	ND	J 190	J 140	< 165	ND	171	190	165	
Di-n-butyl phthalate	84742	< 165	NR	< 165	NR	J 180	NR	< 165	NR	169	180	165	
Fluorene	86737	ND	ND	ND	ND	ND	J 36	ND	ND	NA	NA	NA	2
Phenanthrene	85018	< 165	ND	< 165	ND	570	610	< 165	ND	266	570	165	
Pyrene	129000	< 165	ND	< 165	ND	J 76	J 71	< 165	ND	76	76	76	1
Pyridine	110861	< 330	NR	< 330	NR	J 410	NR	< 330	NR	350	410	330	
2-Methylchrysene	3351324	< 330	NR	< 330	NR	J 77	NR	< 330	NR	77	77	77	1
Naphthalene	91203	ND	ND	ND	ND	ND	ND	ND	J 80	NA	NA	NA	2

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Phenol	108952	< 50	NR	< 50	NR	JB 13	NR	JB 15	NR	14	15	13	1

FCC EQUILIBRIUM CATALYST FINES

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	120,000.0	88,200	73,000.0	53,800	54,000.0	42,800	17,000.0	19,200	66,000.0	120,000.0	17,000.0	
Antimony	7440360	47.0	121	< 6.0	ND	< 6.0	ND	< 6.0	ND	16.3	47.0	6.0	
Arsenic	7440382	11.0	1.1	< 1.0	ND	2.2	0.66	3.3	1.9	4.4	11.0	1.0	
Barium	7440393	160.0	95.4	590.0	461	55.0	39.9	210.0	250	253.8	590.0	55.0	
Beryllium	7440417	13.0	0.69	1.8	0.34	< 0.5	0.36	< 0.5	0.41	4.0	13.0	0.5	
Cadmium	7440439	ND	ND	ND	ND	ND	0.59	ND	0.71	NA	NA	NA	2
Calcium	7440702	1,500.0	NR	2,600.0	NR	2,100.0	NR	1,400.0	NR	1,900.0	2,600.0	1,400.0	
Chromium	7440473	42.0	17.2	57.0	42.8	15.0	15.1	43.0	47.4	39.3	57.0	15.0	
Cobalt	7440484	28.0	15.4	18.0	14.5	< 5.0	5.3	80.0	86.7	32.8	80.0	5.0	
Copper	7440508	23.0	19.9	64.0	62.7	6.9	5.9	19.0	21.6	28.2	64.0	6.9	
Iron	7439896	6,000.0	NR	34,000.0	NR	1,600.0	NR	11,000.0	NR	13,150.0	34,000.0	1,600.0	
Lead	7439921	34.0	11.8	210.0	41.3	7.2	4.7	8.4	6.1	64.9	210.0	7.2	
Manganese	7439965	28.0	19.9	100.0	69.3	11.0	9.9	64.0	71.4	50.8	100.0	11.0	
Molybdenum	7439987	< 6.5	9.1	20.0	22.1	< 6.5	2	< 6.5	8	9.9	20.0	6.5	
Nickel	7440020	900.0	317	780.0	594	73.0	89.3	130.0	145	470.8	900.0	73.0	
Selenium	7782492	< 0.5	NR	3.6	NR	< 0.5	NR	< 0.5	NR	1.3	3.6	0.5	
Sodium	7440235	2,300.0	NR	5,000.0	NR	14,000.0	NR	9,700.0	NR	7,750.0	14,000.0	2,300.0	
Thallium	7440280	< 1.0	NR	3.2	2.2	< 1.0	NR	< 1.0	NR	1.6	3.2	1.0	
Vanadium	7440622	2,600.0	1,230	670.0	582	110.0	105	230.0	247	902.5	2,600.0	110.0	
Zinc	7440666	79.0	84.9	300.0	239	22.0	20	91.0	112	123.0	300.0	22.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R2-FC-01	R2-FC-01S	R4-FC-02	R4-FC-02S	R5-FC-02	R5-FC-02S	R6-FC-02	R6-FC-02S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	110.00	NR	410.00	NR	< 1.30	NR	4.30	NR	131.33	410.00	1.0	
Antimony	7440360	0.89	NR	< 0.30	NR	< 0.30	2.3	< 0.30	ND	0.45	0.89	0.3	
Barium	7440393	ND	0.14	ND	0.017	ND	0.26	ND	0.11	NA	NA	NA	2
Calcium	7440702	< 25.00	NR	100.00	NR	58.00	NR	58.00	NR	60.25	100.00	25.0	
Chromium	7440473	0.24	0.097	0.34	0.074	< 0.05	ND	< 0.05	0.061	0.17	0.34	0.1	
Cobalt	7440484	< 0.25	NR	< 0.25	NR	< 0.25	NR	0.72	NR	0.37	0.72	0.3	
Copper	7440508	0.40	NR	0.33	NR	< 0.13	NR	< 0.13	NR	0.25	0.40	0.1	
Iron	7439896	15.00	NR	14.00	NR	1.60	NR	32.00	NR	15.65	32.00	1.6	
Lead	7439921	ND	ND	ND	ND	ND	ND	ND	0.11	NA	NA	NA	2
Manganese	7439965	0.33	NR	2.70	NR	0.16	NR	0.42	ND	0.91	2.70	0.2	
Mercury	7439976	ND	ND	ND	ND	ND	ND	ND	0.00038	NA	NA	NA	2
Nickel	7440020	3.40	NR	7.50	NR	< 0.20	NR	0.79	NR	2.97	7.50	0.2	
Vanadium	7440622	4.90	NR	< 0.25	NR	< 0.25	NR	< 0.25	NR	1.41	4.90	0.3	
Zinc	7440666	0.61	NR	4.80	NR	0.28	NR	16.00	NR	5.37	16.00	0.3	

Comments:

1. Detection limits greater than the highest detected concentration are excluded from the calculations.
2. Analyte not detected with EPA data, but reported with API data.

Notes:

- B Analyte also detected in the associated method blank.
- J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
- ND Not Detected.
- NA Not Applicable.
- NR Not Reported, or concentration below the method detection limit.

HYDROTREATING CATALYST

Volatile Organics – Method 8260A µg/kg

	CAS No.		R1–TC–01		R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432		500,000		1,900,000	116,383	500,000	2,000	
n–Butylbenzene	104518	<	12,500		ND	11,571	50,000	800	
sec–Butylbenzene	135988	<	12,500		ND	5,936	17,000	800	
tert–Butylbenzene	98066	<	12,500		ND	410	410	410	1
Ethylbenzene	100414		280,000		380,000	72,600	280,000	1,100	
Isopropylbenzene	98828		26,000	J	37,000	11,450	32,000	800	
p–Isopropyltoluene	99876	<	12,500	J	21,000	8,963	25,000	800	
n–Propylbenzene	103651		62,000	J	80,000	22,390	62,000	440	
Methyl ethyl ketone	78933	<	12,500		NR	3,525	9,500	625	1
Toluene	108883		1,300,000		8,000,000	245,754	1,300,000	625	
1,2,3–Trichloropropane	96184		ND	J	24,000	NA	NA	NA	2
1,2,4–Trimethylbenzene	95636		310,000		420,000	96,533	310,000	2,500	
1,3,5–Trimethylbenzene	108678		120,000		160,000	33,677	120,000	1,050	
o–Xylene	95476		370,000		490,000	97,083	370,000	3,500	
m,p–Xylenes	108383 / 106423		550,000		610,000	167,500	550,000	12,000	
Naphthalene	91203	<	12,500		NR	33,432	160,000	140	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R1–TC–01		R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Methylene chloride	75092	<	50		NR	353	950	50	
Benzene	71432		39,000		55,000	7,895	39,000	48	
Ethylbenzene	100414		3,000		NR	709	3,000	50	
Methyl ethyl ketone	78933	<	50		NR	128	520	50	
Toluene	108883		39,000		NR	7,675	39,000	100	
1,2,4–Trimethylbenzene	95636	<	50		NR	83	180	50	
1,3,5–Trimethylbenzene	108678	<	50		NR	92	300	50	
o–Xylene	95476		4,700		NR	1,608	4,700	48	
m,p–Xylene	108383 / 106423		13,000		NR	2,808	13,000	48	
Naphthalene	91203	<	50		NR	75	200	50	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R1–TC–01		R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2–ethylhexyl) phthalate	117817	<	660		NR	258	560	120	1
Di–n–butylphthalate	84742	<	660		NR	110	110	110	1
Benz(a)anthracene	56553	<	660		NR	2,553	14,000	165	
Benzo(a)pyrene	50328	<	660		NR	2,553	14,000	165	
Carbazole	86748	<	1,320		ND	20,400	120,000	92	
Chrysene	218019	<	660		ND	4,220	24,000	165	
Dibenzofuran	132649	<	660		NR	6,536	38,000	72	
Fluoranthene	206440	<	660		ND	5,867	34,000	165	
Fluorene	86737	<	660		NR	21,929	130,000	165	
2,4–Dimethylphenol	105679	J	270	J	1,600	465	830	165	1
2–Methylphenol	95487		6,600	J	2,700	2,543	6,600	165	
3/4–Methylphenol	NA		4,200	J	1,700	1,951	4,200	165	
Phenol	108952		8,200		NR	2,976	8,200	165	
Phenanthrene	85018	<	660		ND	66,909	400,000	165	
Pyrene	129000	<	660		ND	88,578	530,000	165	
1–Methylnaphthalene	90120	J	260		NR	105,315	630,000	260	
2–Methylnaphthalene	91576	J	460		ND	167,089	1,000,000	165	
2–Methylchrysene	3351324	<	1,320		NR	10,107	58,000	330	
Naphthalene	91203	J	1,000		ND	42,134	250,000	140	

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/kg

	CAS No.		R1–TC–01	R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	<	50	NR	12	12	12	1
Bis(2–ethylhexyl) phthalate	117817		270	NR	95	270	22	
Carbazole	86748	<	100	NR	59	59	59	1
Di–n–butyl phthalate	84742	<	50	NR	13	13	13	1
2,4–Dimethylphenol	105679	J	28	NR	50	110	13	
2–Methylphenol	95487	J	80	180	159	430	18	
3/4–Methylphenol (total)	NA	<	50	120	109	790	12	
Phenol	108952	J	28	NR	227	1,000	28	
Fluorene	86737	<	50	NR	14	14	14	1
1–Methylnaphthalene	90120	<	100	NR	113	180	100	
2–Methylnaphthalene	91576	<	50	NR	80	230	50	
Naphthalene	91203	<	50	NR	70	170	50	
Phenanthrene	85018	<	50	NR	16	16	16	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.		R1–TC–01	R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		370,000	374,000	243,333	370,000	150,000	
Antimony	7440360	<	30.0	NR	24.8	60.0	6.0	
Arsenic	7440382		120.0	ND	393.2	1,600.0	42.0	
Beryllium	7440417	<	2.5	ND	2.6	5.7	1.0	
Cadmium	7440439		12.0	NR	3.0	12.0	0.5	
Calcium	7440702	<	2,500.0	NR	2,116.7	5,700.0	500.0	
Chromium	7440473		63.0	ND	20.6	63.0	2.4	
Cobalt	7440484		28,000.0	28,300	5,434.0	28,000.0	25.0	
Copper	7440508		52.0	NR	29.4	52.0	12.5	
Iron	7439896		6,000.0	NR	2,428.3	6,000.0	170.0	
Lead	7439921		3.5	1.9	30.1	130.0	0.8	
Manganese	7439965	<	7.5	19.4	23.9	120.0	1.5	
Molybdenum	7439987		87,000.0	87,900	64,000.0	87,000.0	17,000.0	
Nickel	7440020		66.0	45.2	16,094.3	25,000.0	66.0	
Selenium	7782492		63.0	26.5	68.5	210.0	2.5	
Sodium	7440235	<	2,500.0	NR	3,300.0	10,000.0	500.0	
Thallium	7440280	<	1.0	NR	1.3	2.6	1.0	
Vanadium	7440622		390.0	116	968.3	3,300.0	10.0	
Zinc	7440666	<	10.0	45.6	47.5	140.0	2.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R1–TC–01	R1–TC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		93.00	NR	17.33	93.00	1.00	
Arsenic	7440382	<	0.05	ND	1.10	4.90	0.03	
Cadmium	7440439		0.06	NR	0.03	0.08	0.01	
Calcium	7440702	<	25.00	NR	52.08	200.00	12.50	
Cobalt	7440484		310.00	NR	55.15	310.00	0.13	
Iron	7439896		3.40	NR	13.60	60.00	0.50	
Lead	7439921		ND	0.52	NA	NA	NA	2
Manganese	7439965		0.22	NR	1.03	4.00	0.08	
Molybdenum	7439987		21.00	NR	17.60	48.00	2.60	
Nickel	7440020		0.91	NR	145.62	310.00	0.91	
Selenium	7782492		ND	0.42	NA	NA	NA	2
Vanadium	7440622	<	0.25	NR	1.29	6.60	0.13	
Zinc	7440666	<	0.10	NR	0.60	1.70	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculati
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compou criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

HYDROREFINING CATALYST

Volatile Organics – Method 8260A µg/kg

	CAS No.	R5-TC-01	R5-TC-01S	R7B-RC-01	R7B-RC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	ND	NR	ND	360,000	NA	NA	NA	2
Benzene	71432	4,200	7,100	100,000	190,000	43,733	190,000	4,200	
n-Butylbenzene	104518	J 690	820	J 650	J 3,000	3,760	10,000	650	
sec-Butylbenzene	135988	J 940	1,400	J 510	J 2,400	2,250	5,300	510	
tert-Butylbenzene	98066	ND	540	ND	NR	NA	NA	NA	2
Ethylbenzene	100414	J 1,200	1,700	23,000	39,000	9,667	23,000	1,200	
Isopropylbenzene	98828	< 625	J 260	1,600	5,900	1,113	1,600	625	1
p-Isopropyltoluene	99876	< 625	J 260	< 625	5,300	2,250	5,500	625	
Methylene chloride	75092	< 625	J 200	< 625	NR	1,383	2,900	625	
Naphthalene	91203	< 625	NR	J 960	J 2,900	1,495	2,900	625	
n-Propylbenzene	103651	J 900	1,100	2,000	7,900	1,450	2,000	900	1
Tetrachloroethene	127184	< 625	NR	< 625	NR	3,583	9,500	625	
Toluene	108883	5,700	8,200	190,000	910,000	69,567	190,000	5,700	
1,2,4-Trimethylbenzene	95636	1,900	2,800	6,400	29,000	10,433	23,000	1,900	
1,3,5-Trimethylbenzene	108678	< 625	860	2,600	NR	3,042	5,900	625	
o-Xylene	95476	1,400	2,100	24,000	48,000	10,767	24,000	1,400	
m,p-Xylenes	108383 / 106423	4,100	2,800	78,000	140,000	35,033	78,000	4,100	

TCLP Voatile Organics – Methods 1311 and 8260A µg/L

	CAS No.	R5-TC-01	R5-TC-01S	R7B-RC-01	R7B-RC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	< 50	NR	< 50	NR	70	110	50	
Benzene	71432	110	120	4,200	4,600	1,490	4,200	110	
Ethylbenzene	100414	< 50	NR	140	NR	80	140	50	
Methylene chloride	75092	< 50	NR	< 50	NR	67	100	50	
Toluene	108883	< 50	NR	4,000	NR	1,367	4,000	50	
1,2,4-Trimethylbenzene	95636	< 50	NR	180	NR	93	180	50	
o-Xylene	95476	< 50	NR	150	NR	83	150	50	
m,p-Xylene	108383 / 10642	< 50	NR	530	NR	210	530	50	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.	R5-TC-01	R5-TC-01S	R7B-RC-01	R7B-RC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	< 165	NR	< 1,650	NR	268	370	165	1
Benzo(g,h,i)perylene	191242	460	670	< 1,650	NR	313	460	165	1
Carbazole	86748	ND	J 150	ND	NR	NA	NA	NA	2
Chrysene	218019	ND	J 150	ND	NR	NA	NA	NA	2
Dibenz(a,h)anthracene	53703	ND	J 170	ND	NR	NA	NA	NA	2
Dibenzofuran	132649	< 165	NR	J 1,100	NR	495	1,100	165	
2,4-Dimethylphenol	105679	< 165	NR	5,900	J 1,400	2,152	5,900	165	
Dimethyl phthalate	131113	< 165	NR	< 1,650	NR	208	250	165	1
Di-n-butyl phthalate	87742	< 165	NR	< 1,650	NR	188	210	165	1
2,4-Dinitrophenol	51285	< 800	NR	< 8,000	NR	370	370	370	1
2,4-Dinitrotoluene	121142	< 165	NR	< 1,650	NR	200	240	165	1
Bis(2-ethylhexyl)phthalate	117817	< 165	NR	< 1,650	NR	110	110	110	1
Fluoranthene	206440	ND	950	ND	NR	NA	NA	NA	2
Fluorene	86737	< 165	NR	J 2,800	J 1,100	1,255	2,800	165	
Indeno(1,2,3-cd)pyrene	193395	ND	J 160	ND	NR	NA	NA	NA	2
Isophorone	78591	< 165	NR	< 1,650	NR	150	150	150	1
2-Methylchrysene	3351324	3,400	NR	< 3,300	NR	2,343	3,400	330	
1-Methylnaphthalene	90120	J 520	NR	8,600	NR	4,007	8,600	520	
2-Methylnaphthalene	91576	< 165	J 160	12,000	4,600	5,755	12,000	165	
2-Methylphenol	95487	< 165	NR	5,600	J 1,200	2,008	5,600	165	
3/4-Methylphenol	NA	< 165	NR	J 1,800	NR	712	1,800	165	
Naphthalene	91203	< 165	J 250	J 3,000	J 1,400	1,248	3,000	165	
Phenanthrene	85018	< 165	J 78	J 2,200	J 890	1,168	2,200	165	
Phenol	108952	< 165	NR	J 1,800	NR	710	1,800	165	
Pyrene	129000	3,300	3,500	J 1,600	J 650	1,847	3,300	640	
Pyridine	110861	< 330	NR	< 3,300	NR	4,543	10,000	330	

HYDROREFINING CATALYST

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

Analyte	CAS No.	R5–TC–01	R5–TC–01S	R7B–RC–01	R7B–RC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2–ethylhexyl) phthalate	117817	3,100	NR	< 50	NR	1,056	3,100	18	
Carbazole	86748	< 100	NR	< 100	NR	17	17	17	1
2,4–Dimethylphenol	105679	< 50	NR	220	NR	100	220	30	
Dimethylphthalate	131113	< 50	NR	< 50	NR	34	34	34	1
1–Methylnaphthalene	90120	< 100	NR	< 100	NR	160	260	100	
2–Methylnaphthalene	91576	< 50	NR	< 50	NR	173	420	50	
2–Methylphenol	95487	< 50	ND	290	140	137	290	50	
3/4–Methylphenol (total)	NA	< 50	ND	150	66	88	150	50	
Naphthalene	91203	< 50	NR	< 50	NR	90	170	50	
Phenol	108952	JB 17	NR	160	NR	102	160	17	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

Analyte	CAS No.	R5–TC–01	R5–TC–01S	R7B–RC–01	R7B–RC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	270,000.0	318,000	80,000.0	79,200	173,333	270,000	80,000	
Antimony	7440360	44.0	NR	380.0	428	151.3	380.0	30.0	
Arsenic	7440382	100.0	96.5	650.0	NR	493.3	730.0	100.0	
Beryllium	7440417	43.0	26.8	< 0.5	NR	15.3	43.0	0.5	
Cadmium	7440439	8.7	NR	6.2	24.0	5.5	8.7	2.5	
Chromium	7440473	33.0	28	6.7	NR	14.9	33.0	5.0	
Cobalt	7440484	18,000.0	18,200	8,700.0	21,900	16,900.0	24,000.0	8,700.0	
Copper	7440508	46.0	NR	17.0	23.9	31.7	46.0	17.0	
Iron	7439896	730.0	NR	470.0	NR	766.7	1,100.0	470.0	
Lead	7439921	1.3	NR	< 0.3	NR	1.5	2.8	0.3	
Manganese	7439965	ND	ND	ND	10.7	NA	NA	NA	2
Molybdenum	7439987	74,000.0	66,500	25,000.0	62,900	58,666.7	77,000.0	25,000.0	
Nickel	7440020	14,000.0	21,400	< 8.0	55	4,952.7	14,000.0	8.0	
Selenium	7782492	7.8	ND	1.9	NR	21.2	54.0	1.9	
Thallium	7440280	< 1.0	NR	< 1.0	NR	1.5	2.8	1.0	
Vanadium	7440622	31,000.0	40,600	130.0	376	10,385.0	31,000.0	25.0	
Zinc	7440666	ND	43.5	ND	25.4	NA	NA	NA	2

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

Analyte	CAS No.	R5–TC–01	R5–TC–01S	R7B–RC–01	R7B–RC–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	4.40	NR	< 1.00	NR	2.13	4.40	1.00	
Antimony	7440360	< 0.30	NR	9.60	16.6	3.40	9.60	0.30	
Arsenic	7440382	0.23	0.25	34.00	20.1	13.71	34.00	0.23	
Barium	7440393	ND	0.23	ND	0.07	NA	NA	NA	2
Cadmium	7440439	ND	NR	ND	0.27	NA	NA	NA	2
Cobalt	7440484	55.00	NR	160.00	NR	135.00	190.00	55.00	
Iron	7439896	3.30	NR	6.20	NR	9.50	19.00	3.30	
Lead	7439921	ND	ND	ND	1.6	NA	NA	NA	2
Manganese	7439965	0.17	NR	< 0.08	NR	0.18	0.29	0.08	
Molybdenum	7439987	< 1.00	NR	13.00	NR	10.33	17.00	1.00	
Nickel	7440020	67.00	NR	0.73	NR	26.24	67.00	0.73	
Vanadium	7440622	3.30	NR	< 0.25	NR	1.27	3.30	0.25	
Zinc	7440666	0.39	NR	< 0.10	NR	0.20	0.39	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

SCOT CATALYST from SULFUR COMPLEX

Volatile Organics – Method 8260A $\mu g/kg$

	CAS No.		R7B-SC-01		R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432	<	625	J	130	33	80	5	1
n-Butylbenzene	104518	J	700		NR	243	700	5	
Trichlorofluoromethane	75694	<	625		NR	27	29	25	1
Toluene	108883	<	625	J	360	15	24	5	1
1,2,4-Trimethylbenzene	95636		7,500		590	2,510	7,500	5	
1,3,5-Trimethylbenzene	108678		3,300	J	290	1,117	3,300	5	
o-Xylene	95476	J	1,040	J	230	356	1,040	5	
m,p-Xylenes	108383 /106423		2,500	J	260	856	2,500	5	
4-Methyl-2-pentanone	108101	<	625		NR	128	250	5	1
Methyl ethyl ketone	78933	<	625		NR	233	460	5	1
Methylene chloride	75092	<	625	J	110	33	60	5	1

TCLP Volatile Organics – Methods 1311 and 8260A $\mu g/L$

	CAS No.		R7B-SC-01		R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Methylene chloride	75092	<	50		NR	567	1,600	50	

Semivolatile Organics – Method 8270B $\mu g/kg$

	CAS No.		R7B-SC-01		R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	J	88		NR	184	300	88	
Butyl benzyl phthalate	85687		ND	J	84	NA	NA	NA	2
Di-n-butyl phthalate	84742	J	120		NR	110	120	90	
Pyridine	110861		ND	J	140	NA	NA	NA	2

TCLP Semivolatile Organics – Methods 1311 and 8270B $\mu g/L$

	CAS No.		R7B-SC-01		R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis (2-ethylhexyl)phthalate	117817	<	50		NR	208	540	35	
Di-n-butyl phthalate	84742	<	50		NR	31	31	31	1
Pyridine	110861		240		390	147	240	100	

SCOT CATALYST from SULFUR COMPLEX

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.		R7B-SC-01	R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		360,000	252,000	223,333.3	360,000.0	110,000.0	
Antimony	7440360		20.0	NR	13.3	20.0	6.0	
Arsenic	7440382	<	20.0	NR	19.3	28.0	10.0	
Beryllium	7440417		2.9	ND	1.3	2.9	0.5	
Cadmium	7440439		9.4	NR	7.2	9.4	5.7	
Chromium	7440473		13.0	NR	8.0	13.0	4.8	
Cobalt	7440484		19,000.0	19,700	14,333.3	19,000.0	11,000.0	
Copper	7440508		33.0	21.6	25.3	33.0	14.0	
Iron	7439896		3,500.0	NR	1,810.0	3,500.0	230.0	
Manganese	7439965		54.0	50.6	19.6	54.0	1.5	
Molybdenum	7439987		64,000.0	63,700	42,333.3	64,000.0	25,000.0	
Nickel	7440020		73.0	48.2	70.3	120.0	18.0	
Selenium	7782492	<	2.5	NR	1.4	2.2	0.5	1
Sodium	7440235	<	500.0	NR	1,433.3	2,500.0	500.0	
Vanadium	7440622		210.0	319	180.7	260.0	72.0	
Zinc	7440666		ND	36.3	NA	NA	NA	2

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R7B-SC-01	R7B-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		32.00	NR	23.67	32.00	17.00	
Arsenic	7440382		ND	0.61	NA	NA	NA	2
Cadmium	7440439		0.20	0.045	0.08	0.20	0.03	
Chromium	7440473		0.13	NR	0.08	0.13	0.05	
Cobalt	7440484		460.00	NR	248.67	460.00	66.00	
Iron	7439896	<	0.50	NR	2.43	6.30	0.50	
Lead	7439921		ND	3.5	NA	NA	NA	2
Manganese	7439965		0.99	NR	0.47	0.99	0.08	
Molybdenum	7439987		480.00	NR	316.33	480.00	39.00	
Nickel	7440020		0.54	NR	0.44	0.58	0.20	
Selenium	7782492		ND	1.1	NA	NA	NA	2
Vanadium	7440622		1.90	NR	1.18	1.90	0.25	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identificatic criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

Volatile Organics – Method 8260A µg/kg

	CAS No.		R2-CR-01		R2-CR-01S		R7B-CR-01		R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641		ND		ND		ND		1,700	NA	NA	NA	2
Benzene	71432	<	25		570		2,300		2,300	4,992	26,000	25	
n-Butylbenzene	104518	<	25		NR		220		NR	11,032	57,000	22	
sec-Butylbenzene	135988	<	25		NR		110		NR	4,264	23,000	22	
Ethylbenzene	100414	<	25		ND		1,900		690	13,262	51,000	25	
2-Hexanone	591786	<	25		NR	<	25		NR	3,954	23,000	22	
Isopropylbenzene	98828	<	25		NR		180		NR	5,498	27,000	25	
n-Propylbenzene	103651	<	25		ND		570	J	240	10,222	60,000	25	
Toluene	108883	<	25		550		11,000		7,800	11,789	37,000	25	
1,2,4-Trimethylbenzene	95636		2,600		2,300		4,000		760	56,700	310,000	25	
1,3,5-Trimethylbenzene	108678		580		600		590	J	250	18,726	91,000	25	
o-Xylene	95476		110	J	170		5,100		1,800	27,490	110,000	25	
m,p-Xylenes	108383 / 106423		220	J	150		9,000		1,300	42,124	170,000	25	
Methyl ethyl ketone	78933	<	25		NR		260		NR	705	3,200	25	
Methylene chloride	75092	<	25		NR	<	25		NR	32	55	22	1
Naphthalene	91203		1,900		1,100		430		ND	2,084	9,500	22	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R2-CR-01		R2-CR-01S		R7B-CR-01		R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432	<	50		370	<	50		120	638	3,000	42	
Ethylbenzene	100414	<	50		NR	<	50		NR	144	470	50	
Toluene	108883	<	50		NR		440		NR	1,010	4,000	50	
Trichloroethene	79016		ND		ND		ND	J	10	NA	NA	NA	2
1,2,4-Trimethylbenzene	95636		110		NR		140		NR	242	610	50	
1,3,5-Trimethylbenzene	108678	<	50		NR	<	50		NR	78	160	50	
o-Xylene	95476	<	50		NR		210		NR	330	1,200	50	
m,p-Xylene	108383/106423	<	50		NR		340		NR	506	1,500	50	
Methylene chloride	75092	<	50		NR	<	50		NR	256	930	50	
Naphthalene	91203		120		NR	<	50		NR	67	120	50	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R2-CR-01		R2-CR-01S		R7B-CR-01		R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Anthracene	120127	<	165		NR	<	165		NR	140	140	140	1
Bis(2-ethylhexyl)phthalate	117817	<	165		NR	<	165		NR	328	940	165	
Butyl benzyl phthalate	85687	<	165		NR	<	165		NR	189	310	165	
Di-n-butyl phthalate	87742	<	165		NR	<	165		NR	158	230	67	1
Benz(a)anthracene	56553		4,500		7,300	<	165		ND	970	4,500	165	
Benzofluoranthene (total)	NA		8,300		7,100	<	165		ND	1,603	8,300	165	
Benzo(g,h,i)perylene	191242		6,500		9,800	<	165		ND	1,303	6,500	165	
Benzo(a)pyrene	50328		2,900		690	<	165		ND	703	2,900	165	
Dibenz(a,h)anthracene	53703	J	260		NR	<	165		NR	184	260	165	1
2,4-Dimethylphenol	105679	<	165		NR	<	165		NR	2,638	15,000	165	
Chrysene	218019		4,000		5,600	<	165		ND	887	4,000	165	
Fluoranthene	206440		5,000		6,000	<	165		ND	1,053	5,000	165	
Fluorene	86737	<	165		NR	<	165		NR	78	78	78	1
Indeno(1,2,3-cd)pyrene	193395		4,600		5,400	<	165		ND	987	4,600	165	
Isophorone	78591	<	165		ND		650	J	5,000	262	650	165	1
1-Methylnaphthalene	90120		2,000		NR	<	330		NR	1,098	2,400	330	
2-Methylnaphthalene	91576		3,000		5,400	J	91		ND	3,020	11,000	91	
2-Methylphenol	95487	<	165		NR	J	270		NR	4,844	25,000	165	
3/4-Methylphenol (total)	NA	<	165		NR		330		NR	4,888	24,000	165	
Naphthalene	91203		2,100		2,800	J	190		ND	3,064	8,900	130	
Phenanthrene	85018		14,000		10,000	<	165		ND	2,640	14,000	160	
Phenol	108952	<	165		NR	<	165		NR	4,043	21,000	165	
Pyrene	129000		4,200		4,700	<	165		ND	920	4,200	165	
2-Methylchrysene	3351324	J	370		NR	<	330		NR	336	370	330	1

REFORMING CATALYST

TCLP Semivolatile Organics – Methods 1311 and 8270B μ/L

	CAS No.		R2-CR-01	R2-CR-01S		R7B-CR-01	R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	<	50	NR	<	50	NR	52	61	50	
Di-n-butyl phthalate	84742	<	50	NR	<	50	NR	46	46	46	1
2,4-Dimethylphenol	105679	<	50	NR	<	50	NR	116	460	50	
1-Methylnaphthalene	90120	J	34	NR	<	100	NR	25	34	16	1
2-Methylnaphthalene	91576	J	43	NR	<	50	NR	43	43	43	1
2-Methylphenol	95487	<	50	NR	<	50	NR	145	620	50	
3/4-Methylphenol (total)	NA	<	50	NR	<	50	NR	123	490	50	
Naphthalene	91203	J	59	NR	<	50	NR	46	59	27	
Phenanthrene	85018	J	35	NR	<	50	NR	35	35	35	1
Phenol	108952	<	50	NR	<	50	NR	105	380	50	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

			R2-CR-01	R2-CR-01S		R7B-CR-01	R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		230,000.0	47,300		460,000.0	242,000	250,000	460,000	150,000	
Antimony	7440360	<	12.0	NR	<	6.0	NR	8.6	17.0	6.0	
Arsenic	7440382	<	10.0	1	<	20.0	ND	19.3	45.0	10.0	
Barium	7440393		ND	18		ND	ND	NA	NA	NA	2
Chromium	7440473		44.0	229		25.0	33.8	126.5	550.0	25.0	
Cobalt	7440484	<	10.0	ND	<	5.0	26.6	466.3	2,900.0	5.0	
Copper	7440508	<	5.0	73		26.0	ND	1,374.8	8,100.0	2.5	
Iron	7439896		460.0	NR		21,000.0	NR	13,060.0	51,000.0	120.0	
Lead	7439921	<	3.0	124	<	0.6	1.8	27.7	160.0	0.3	
Manganese	7439965	<	3.0	73		43.0	35.7	43.7	160.0	1.5	
Molybdenum	7439987	<	13.0	164		18.0	73.6	1,678.6	10,000.0	6.5	
Nickel	7440020	<	8.0	NR		12.0	NR	73.7	220.0	4.0	
Selenium	7782492	<	5.0	NR	<	2.5	NR	4.2	14.0	0.5	
Sodium	7440235	<	1,000.0	NR	<	500.0	NR	2,166.7	10,000.0	500.0	
Vanadium	7440622	<	10.0	ND	<	25.0	17.4	21.0	78.0	5.0	
Zinc	7440666	<	4.0	NR	<	2.0	NR	466.3	2,900.0	2.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R2-CR-01	R2-CR-01S		R7B-CR-01	R7B-CR-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		26.00	NR		360.00	NR	141.72	360.00	5.3	
Antimony	7440360		ND	NR		ND	0.17	NA	NA	NA	2
Arsenic	7440382		ND	0.19		ND	ND	NA	NA	NA	2
Barium	7440393		ND	0.061		ND	0.37	NA	NA	NA	2
Cadmium	7440439		ND	ND		ND	0.1	NA	NA	NA	2
Chromium	7440473	<	0.05	0.051		0.19	0.2	0.10	0.23	0.05	
Cobalt	7440484	<	0.25	NR	<	0.25	NR	18.04	95.00	0.25	
Copper	7440508	<	0.13	NR	<	0.13	NR	10.30	61.00	0.13	
Iron	7439896	<	0.50	NR		8.90	NR	2.35	8.90	0.50	
Lead	7439921	<	0.02	ND		1.10	0.72	0.48	1.70	0.02	
Manganese	7439965	<	0.08	NR		1.60	NR	0.63	1.90	0.08	
Nickel	7440020	<	0.20	NR		0.65	NR	0.93	3.60	0.20	
Selenium	7782492	<	0.03	NR	<	0.03	NR	0.03	0.06	0.03	
Zinc	7440666		0.61	NR	<	0.10	NR	16.79	99.00	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

SLUDGE from SULFURIC ACID ALKYLATION

Volatile Organics – Method 8260A µg/kg

	CAS No.		R8B–SS–01		R8B–SS–01S
Acetone	67641		7,000		2,300
Ethylbenzene	100414	J	150	<	250
Toluene	108883	J	160	<	250
1,2,4–Trimethylbenzene	95636	J	280	J	180
m,p–Xylenes	108383 / 106423	J	170	<	250
Naphthalene	91203	J	180	<	250

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R8B–SS–01		R8B–SS–01S
Acetone	67641		810		NR
Methylene chloride	75092	B	200		NR
Methyl ethyl ketone	78933		120		54

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R8B–SS–01		R8B–SS–01S
Bis(2–ethylhexyl)phthalate	117817		1,000		1,300
Di–n–butyl phthalate	84742	J	250	<	850
7,12–Dimethylbenz(a)anthracene	57976		ND	J	300
Benz(a)anthracene	56553	J	270	J	220
Benzo(g,h,i)perylene	191242	J	250	J	140
Benzo(a)pyrene	50328	J	190	<	850
Chrysene	218019	J	460	J	420
Fluoranthene	206440		ND	J	230
Fluorene	86737	J	210	J	390
Phenanthrene	85018	J	680		1,300
Pyrene	129000		2,200		1,800
1–Methylnaphthalene	90120	J	1,400		2,700
2–Methylnaphthalene	91576		2,200		6,300
2–Methylchrysene	3351324	J	340		NR
Naphthalene	91203	J	290	J	830
N–Nitrosodiphenylamine	86306		ND	J	940

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.		R8B–SS–01		R8B–SS–01S
1–Methylnaphthalene	90120	J	24		NR
2–Methylnaphthalene	91576	J	31		NR
Naphthalene	91203	J	30		NR

SLUDGE from SULFURIC ACID ALKYLATION

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R8B-SS-01		R8B-SS-01S
Aluminum	7429905	1,100		1,390
Antimony	7440360	5.8		3.1
Arsenic	7440382	2.4		2.8
Barium	7440393	3.2		141
Cadmium	7440439	0.09	<	0.25
Calcium	7440702	16,000		NR
Chromium	7440473	190		238
Cobalt	7440484	3.3		4.0
Copper	7440508	37.0		68.0
Iron	7439896	6,800.00		NR
Lead	7439921	23.0		53.7
Magnesium	7439954	670		NR
Manganese	7439965	45.0		55.1
Mercury	7439976	0.035		0.16
Moylbdenum	7439987	1.7		3.1
Nickel	7440020	280		359
Potassium	7440097	200		NR
Sodium	7440235	10,000		NR
Vanadium	7440622	3.4		3.9
Zinc	7440666	58.0		54.1

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R8B-SS-01	R8B-SS-01S
Aluminum	7429905	87.0	NR
Antimony	7440360	ND	0.29
Barium	7440393	ND	0.11
Calcium	7440439	430.0	NR
Chromium	7440473	15.0	28.4
Copper	7440508	1.4	NR
Iron	7439896	520.0	NR
Lead	7439921	1.1	0.71
Magnesium	7439954	56.0	NR
Manganese	7439965	3.7	NR
Nickel	7440020	17.0	NR
Zinc	7440666	4.0	NR

Notes:

- B Analyte also detected in the associated method blank.
- J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
- ND Not Detected.
- NR Not Reported.

Volatile Organics – Method 8260A µg/kg

	CAS No.		R3–HS–01		R3–HS–01S		R9–HS–01		R9–HS–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	<	12,500		ND		16,000		24,000	9,140	16,000	2,600	
Benzene	71432	J	6,100	J	4,100	<	625		ND	4,336	14,000	313	
Chlorobenzene	108907	<	12,500		NR	<	625		NR	847	1,600	313	1
n–Butylbenzene	104518	<	12,500		31,000		1,900		7,800	827	1,900	313	1
Crotonaldehyde	4170303		82,000		NR	<	625		NR	16,843	82,000	313	
sec–Butylbenzene	135988	J	20,000		ND	<	625	J	2,400	4,436	20,000	290	
tert–Butylbenzene	98066	<	12,500		NR	<	625		NR	623	680	560	1
trans–1,3–Dichloropropene	10061026		ND		ND		ND		49,000	NA	NA	NA	2
Ethylbenzene	100414		73,000		50,000	<	625	J	1,200	15,072	73,000	350	
Isopropylbenzene	98828	J	14,000	J	9,100	<	625	J	4,800	3,243	14,000	313	
p–Isopropyltoluene	99876	J	13,000		23,000	<	625		ND	3,043	13,000	313	
Methylene chloride	75092		ND	BJ	2,000		ND		ND	NA	NA	NA	2
Methyl ethyl ketone	78933	<	12,500		NR		3,400		NR	1,609	3,400	313	1
n–Propylbenzene	103651		87,000		40,000	<	625	J	2,000	13,849	87,000	313	
Toluene	108883		85,000		61,000	<	625	J	2,900	17,436	85,000	190	
1,2,4–Trimethylbenzene	95636		488,000		360,000		12,000		41,000	101,165	488,000	625	
1,3,5–Trimethylbenzene	108678		143,000		100,000		6,700		22,000	30,465	143,000	625	
o–Xylene	95476		127,000		91,000		1,600	J	3,600	25,971	127,000	220	
m,p–Xylenes	108383/106423		352,000		110,000		3,700	J	4,700	71,597	352,000	460	
Naphthalene	91203		37,000		99,000		1,400	J	4,000	8,064	37,000	313	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R3–HS–01		R3–HS–01S		R9–HS–01		R9–HS–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	<	50		NR		1,290		NR	582	1,290	50	
Benzene	71432		180		160	<	50		ND	76	180	50	
Ethylbenzene	100414	B	530		NR	<	50		NR	148	530	50	
n–Propylbenzene	103651		120		NR	<	50		NR	64	120	50	
Toluene	108883	B	1,200		NR	<	50		NR	280	1,200	50	
Methylene chloride	75092	<	50		NR		370		NR	548	2,000	50	
Methyl ethyl ketone	78933	<	50		ND	<	50		240	75	150	50	
1,2,4–Trimethylbenzene	95636		1,300		NR	<	50		NR	380	1,300	50	
1,3,5–Trimethylbenzene	108678		1,100		NR	<	50		NR	280	1,100	50	
o–Xylene	95476	B	1,100		NR	<	50		NR	280	1,100	50	
m,p–Xylene	108383 / 106423	B	460		NR	<	50		NR	138	480	50	
Naphthalene	91203		460		NR	<	50		NR	127	460	23	

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R3–HS–01		R3–HS–01S		R9–HS–01		R9–HS–01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzenethiol	108985		ND	E	180,000		ND		ND	NA	NA	NA	2
Bis(2–ethylhexyl)phthalate	117817	J	2,100		ND	<	5,157	J	33,000	1,332	2,100	165	1
Fluorene	86737	J	2,900		NR	<	5,157		NR	1,532	2,900	165	1
Indene	95136	J	3,300		NR	<	5,157		NR	1,632	3,300	165	1
Phenanthrene	85018	J	4,500		NR	<	5,157		NR	2,481	4,500	1,000	1
Phenol	108952		120,000	E	220,000	<	5,157		ND	25,677	120,000	165	
1–Methylnaphthalene	90120		98,000	J	5,000	<	10,313		ND	23,448	98,000	2,000	
2–Methylnaphthalene	91576		180,000		10,000	<	5,157	J	15,000	38,724	180,000	1,000	
2–Methylphenol	95487		16,000		46,000	<	5,157		ND	4,677	16,000	165	
3/4–Methylphenol (total)	NA		32,000		86,000	<	5,157		ND	8,077	32,000	165	
Naphthalene	91203		110,000	J	6,100	J	4,800		ND	23,973	110,000	1,000	

HF ALKYLATION SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.		R3-HS-01		R3-HS-01S		R9-HS-01		R9-HS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis(2-ethylhexyl)phthalate	117817	J	10		NR	JB	13		NR	12	13	10	1
Di-n-butylphthalate	84742	<	50		NR	<	50		NR	64	120	50	
2,4-Dimethylphenol	105679	J	71		NR	<	50		NR	54	71	50	
2-Methylphenol	95487		830		2,500	<	50		ND	206	830	50	
3/4-Methylphenol (total)	NA		1,200		4,500	<	50		ND	280	1,200	50	
1-Methylnaphthalene	90120	J	97		NR	J	21		NR	46	97	19	1
2-Methylnaphthalene	91576		160		NR	<	50		NR	68	160	28	
Naphthalene	91203		320		NR	<	50		NR	98	320	22	
Phenol	108952		4,100		NR	<	50		NR	860	4,100	50	
Indene	95136	J	12		NR	<	50		NR	12	12	12	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.		R3-HS-01		R3-HS-01S		R9-HS-01		R9-HS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		4,400.0		1,100		980.0		1,030	2,580.6	6,000.0	23.0	
Antimony	7440360	<	6.0		NR	<	6.0		NR	9.7	30.0	0.3	
Arsenic	7440382		5.7		0.69	<	1.0		ND	3.4	5.7	0.2	
Barium	7440393		85.0		22.9	<	20.0		5	29.2	85.0	1.0	
Calcium	7440702		76,000.0		NR		87,000.0		NR	105,500.0	200,000.0	35,000.0	
Chromium	7440473		59.0		17		2.4		3.7	13.9	59.0	0.1	
Cobalt	7440484		710.0		205	<	5.0		1.4	145.1	710.0	0.3	
Copper	7440508		300.0		66.1		84.0	B	95	84.1	300.0	0.7	
Iron	7439896		26,000.0		NR		720.0		NR	5,903.2	26,000.0	26.0	
Lead	7439921		110.0		31.5		1.7		ND	22.7	110.0	0.0	
Magnesium	7439954		3,700.0		NR		1,100.0		NR	1,316.6	3,700.0	83.0	
Manganese	7439965		180.0		62.3		33.0		37	51.3	180.0	1.0	
Nickel	7440020		730.0		215		220.0		203	217.6	730.0	4.1	
Potassium	7440097		4,100.0		NR	<	500.0		NR	7,825.0	34,000.0	25.0	
Selenium	7782492		ND		2.1		ND		ND	NA	NA	NA	2
Sodium	7440235		8,600.0		NR		4,100.0		NR	10,000.0	19,000.0	4,100.0	
Vanadium	7440622		16.0		2.5	<	5.0		2.9	6.5	16.0	0.3	
Zinc	7440666		130.0	B	39.1		7.5		4.9	31.7	130.0	1.1	

TCLP Metals – Methods 1311, 6010, 7060 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R3-HS-01		R3-HS-01S		R9-HS-01		R9-HS-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	<	1.00		NR	<	1.00		NR	1.84	5.20	1.00	
Antimony	7440360	<	0.30		NR	<	0.30		NR	0.36	0.62	0.30	
Barium	7440393				1.6		ND		0.93	NA	NA	NA	2
Cadmium	7440439				0.016		ND		ND	NA	NA	NA	2
Calcium	7440702		670.00		NR	<	25.00		NR	529.00	2,000.00	25.00	
Copper	7440508	<	0.13		NR		0.73		NR	0.29	0.73	0.13	
Iron	7439896		3.70		NR	<	0.50		NR	1.60	3.70	0.50	
Manganese	7439965		0.71		NR	<	0.08		NR	0.36	0.71	0.08	
Nickel	7440020	<	0.20		NR		0.46		NR	1.17	4.30	0.20	
Potassium	7440097		150.00		NR	<	25.00		NR	365.00	1,600.00	25.00	
Zinc	7440666		0.31		NR		0.22		NR	0.34	0.46	0.22	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
E Reported concentration exceeds the calibration range.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

OFF-SPEC PRODUCT and FINES from THERMAL PROCESS

Volatile Organics – Method 8260A µg/kg

Compound	CAS No.		R6-TP-01		R6-TP-01S		R6A-TP-01		R6A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432	<	5	J	430	<	25	J	900	467	1,500	5	
n-Butylbenzene	104518	<	5		NR		82	<	250	593	2,200	5	
Ethylbenzene	100414	<	5		NR	J	25	<	250	352	810	5	
p-Isopropyltoluene	99876	<	5		NR	J	38	<	250	388	1,000	5	
Methylene chloride	75092		ND	J	120		ND	BJ	160	NA	NA	NA	2
n-Propylbenzene	103651	<	5		NR	<	25	<	250	417	1,200	5	
Toluene	108883	<	5		870	J	19	J	350	683	2,800	5	
1,2,4-Trimethylbenzene	95636	<	5		NR		270	J	250	1,631	8,200	5	
1,3,5-Trimethylbenzene	108678	<	5		NR		140	J	140	721	2,900	5	
o-Xylene	95476	<	5		NR		83	J	130	640	2,500	5	
m,p-Xylenes	108383 / 106423	<	5	J	200		93	J	320	624	3,200	5	
Naphthalene	91203	<	5		600		270	J	350	1,030	3,800	5	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

Compound	CAS No.		R6-TP-01		R6-TP-01S		R6A-TP-01		R6A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzene	71432		ND		NR		ND		250	NA	NA	NA	2
Methylene chloride	75092	<	50		NR	<	50		NR	140	340	50	
Methyl ethyl ketone	78933	<	50		NR	<	50		NR	83	250	50	

Semivolatile Organics – Method 8270B µg/kg

Compound	CAS No.		R6-TP-01		R6-TP-01S		R6A-TP-01		R6A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	<	825		NR	<	4,125	J	480	2,595	11,000	165	
Anthracene	120127		1,900	J	1,200	J	2,700	J	1,600	2,861	9,400	165	
Benz(a)anthracene	56553		28,000		16,000		8,700		4,800	11,976	28,000	165	
Benzofluoranthene (total)	NA		28,000		13,000	J	8,100	J	3,100	9,028	28,000	165	
Benzo(g,h,i)perylene	191242		21,000		7,000		19,000		12,000	9,344	21,000	165	
Benzo(a)pyrene	50328		33,000		14,000		13,000		6,400	11,628	33,000	165	
bis(2-Ethylhexyl)phthalate	117817	<	825		NR	<	4,125	<	2,000	16,349	87,000	165	
Carbazole	86748		6,900	J	1,400	<	8,250	J	570	3,256	6,900	330	1
Chrysene	218019		65,000		31,000		11,000		5,300	24,028	55,000	165	
Dibenz(a,h)anthracene	53703		14,000		5,700	J	3,000	J	2,000	4,532	14,000	165	
Dibenzofuran	132649	<	825	J	190	<	4,125	<	2,000	2,228	6,400	165	
7,12-Dimethylbenz(a)anthracene	57976	<	825		NR	<	4,125	<	2,000	605	1,200	165	1
Fluoranthene	206440		3,600		2,600	<	4,125	J	890	2,565	4,300	165	
Fluorene	86737	J	900	J	540	<	4,125	J	1,000	3,462	14,000	165	
Indeno(1,2,3-cd)pyrene	193395		6,200		2,800	J	3,000	J	1,600	3,008	6,200	165	
Phenanthrene	85018		10,000		5,800	J	7,500		4,800	13,911	58,000	165	
Pyrene	129000		27,000		11,000		14,000		6,800	10,911	27,000	165	
1-Methylnaphthalene	90120	J	890	J	350	J	4,400	J	2,900	10,858	58,000	330	
2-Methylnaphthalene	91576		3,400		2,200	J	8,200		7,000	17,694	39,000	165	
2-Methylchrysene	3351324		25,000		NR	J	11,000		NR	19,422	47,000	330	
Naphthalene	91203		3,100		2,000	J	2,900	J	2,800	3,611	12,000	165	

OFF-SPEC PRODUCT and FINES from THERMAL PROCESS

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.		R6-TP-01	R6-TP-01S		R8A-TP-01		R8A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Di-n-butylphthalate	84742	JB	14	NR	<	50		NR	41	50	14	
Benz(a)anthracene	56553	<	50	NR	<	50		NR	13	13	13	1
Benzo(a)pyrene	50328	<	50	NR	<	50		NR	10	10	10	1
Bis(2-ethylhexyl) phthalate	117817	<	50	NR		230		NR	75	230	20	
Chrysene	218019	<	50	NR	<	50		NR	35	35	35	1
2-Methylchrysene	3351324	<	100	NR	<	100		NR	15	15	15	1
1-Methylnaphthalene	90120	<	100	NR	<	100		NR	21	21	21	1
2-Methylnaphthalene	91576	<	50	NR	<	50		NR	23	23	23	1
Phenol	108952	JB	17	NR	<	50		NR	17	17	17	1

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.		R6-TP-01	R6-TP-01S		R8A-TP-01		R8A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		64.0	52		87.0		98.2	56.8	130.0	20.0	
Barium	7440393		ND	6.8		ND		4.6	NA	NA	NA	2
Beryllium	7440417		ND	NR		ND		0.22	NA	NA	NA	2
Chromium	7440473	<	1.0	NR	<	1.0		1.6	1.3	3.0	1.0	
Cobalt	7440484		ND	1.8		ND		2.8	NA	NA	NA	2
Copper	7440508	<	2.5	NR	<	2.5	<	1.0	4.7	13.0	2.5	
Iron	7439896		230.0	NR		190.0		NR	275.0	800.0	10.0	
Lead	7439921		2.5	NR		0.8		0.65	1.5	3.7	0.3	
Manganese	7439965	<	1.5	1.8	<	1.5		1.6	2.4	7.0	1.5	
Mercury	7439976	<	0.05	NR	<	0.05	<	0.05	0.08	0.10	0.1	
Molybdenum	7439987		ND	NR		ND		26.6	NA	NA	NA	2
Nickel	7440020		46.0	17.2		12.0		20.0	39.3	120.0	8.5	
Selenium	7782492	<	0.5	NR	<	0.5	<	0.8	0.7	1.4	0.5	
Vanadium	7440622		61.0	34.5		70.0		107	109.5	310.0	28.0	
Zinc	7440666		7.8	5.9		7.5		7.2	9.5	20.0	2.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R6-TP-01	R6-TP-01S		R8A-TP-01		R8A-TP-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Barium	7440393		ND	0.38		ND		0.07	NA	NA	NA	2
Iron	7439896	<	0.50	NR	<	0.50		NR	0.65	1.40	0.50	
LEAD	7439921	<	0.015	NR	<	0.015	<	0.025	0.02	0.03	0.02	
Zinc	7440666		0.75	NR		0.31		NR	0.43	0.75	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

SPENT CAUSTIC from LIQUID TREATING

Volatile Organics – Method 8260A µg/L

	CAS No.	R3-LT-01	R3-LT-01S	R3-LT-02	R3-LT-02S	R6-LT-01	R6-LT-01S	R13-LT-01	R13-LT-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	15,000	10,000	< 500	ND	< 5,000	ND	390,000	B 310,000	69,542	390,000	50	
Benzene	71432	J 90	ND	< 500	ND	< 5,000	J 2,600	J 420	J 440	652	2,200	50	1
n-Butylbenzene	104518	ND	J 240	ND	ND	ND	J 4,500	ND	ND	NA	NA	NA	2
sec-Butylbenzene	135988	ND	ND	ND	ND	ND	J 3,700	ND	ND	NA	NA	NA	2
Carbon disulfide	75150	< 500	NR	1,400	NR	< 5,000	NR	< 250	NR	540	1,400	50	1
Ethylbenzene	100414	J 710	J 390	< 500	ND	11,000	6,500	640	J 600	2,272	11,000	50	
Isopropylbenzene	98828	ND	ND	ND	ND	ND	J 3,900	ND	ND	NA	NA	NA	2
p-Isopropyltoluene	99876	ND	J 190	ND	ND	ND	J 4,200	ND	ND	NA	NA	NA	2
n-Propylbenzene	103651	J 660	J 350	< 500	ND	< 5,000	5,800	J 360	1,700	215	360	50	
Toluene	108883	J 740	J 450	J 200	J 100	21,000	19,000	920	J 1,100	4,485	21,000	50	
1,2,4-Trimethylbenzene	95636	8,500	5,500	< 500	ND	51,000	44,000	2,200	2,300	10,534	51,000	50	
1,3,5-Trimethylbenzene	108678	1,600	1,100	< 500	ND	20,000	18,000	740	J 720	3,898	20,000	50	
o-Xylene	95476	2,600	1,400	< 500	ND	21,000	18,000	1,500	1,600	4,423	21,000	50	
m,p-Xylenes	108383 / 106423	4,000	980	J 220	ND	49,000	21,000	3,000	1,400	9,778	49,000	50	
Methylene chloride	75092	ND	BJ 160	ND	BJ 160	ND	ND	ND	ND	NA	NA	NA	2
Methyl ethyl ketone	78933	6,000	NR	570	NR	11,000	NR	1,400	NR	3,653	11,000	50	
Naphthalene	91203	2,900	3,200	< 500	ND	29,000	26,000	7,600	11,000	7,025	29,000	50	
4-Methyl-2-pentanone	108101	< 500	NR	< 500	NR	< 5,000	NR	760	NR	466	760	50	1
Styrene	100425	< 500	NR	< 500	NR	< 5,000	NR	3,300	NR	970	3,300	50	1

Semivolatile Organics – Method 8270B µg/L

	CAS No.	R3-LT-01	R3-LT-01S	R3-LT-02	R3-LT-02S	R6-LT-01	R6-LT-01S	R13-LT-01	R13-LT-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
2,4-Dimethylphenol	105679	2,570,000	J 2,300,000	J 24,000	J 8,600	340,000	250,000	E 450,000	E 630,000	615,963	2,570,000	1,900	
Fluoranthene	206440	ND	ND	ND	ND	ND	J 1,500	ND	ND	NA	NA	NA	2
Indene	95136	< 50,000	NR	< 25,000	NR	< 1,250	NR	J 5,800	NR	2,483	5,800	400	1
Isophorone	78591	< 50,000	NR	< 25,000	NR	< 1,250	NR	16,000	NR	5,975	16,000	400	1
2-Methylphenol	95487	32,400,000	E 22,000,000	229,000	E 130000	96,000	120,000	E 150,000	E 1,300,000	5,797,433	32,400,000	9,600	
3/4-Methylphenol	NA	54,600,000	E 37,000,000	510,000	E 340000	170,000	240,000	77,000	E 1,500,000	10,144,350	54,600,000	9,100	
Pentachlorophenol	87865	ND	ND	ND	ND	ND	J 1,300	ND	ND	NA	NA	NA	2
Phenanthrene	85018	ND	ND	ND	ND	ND	14,000	ND	ND	NA	NA	NA	2
Phenol	108952	92,600,000	E 56,000,000	1,600,000	E 1,600000	24,000	J 60,000	J 5,100	630,000	19,372,933	92,600,000	5,100	
Benzenethiol	108985	1,130,000	ND	6,070,000	750000	< 2,500	ND	J 4,400	540,000	1,434,550	6,070,000	400	
1-Methylnaphthalene	90120	< 100,000	ND	< 50,000	ND	33,000	41,000	< 3,425	ND	10,606	33,000	800	1
2-Methylnaphthalene	91576	< 50,000	ND	< 25,000	ND	22,000	56,000	< 1,713	ND	7,203	22,000	400	1
Naphthalene	91203	< 50,000	ND	< 25,000	ND	26,000	31,000	15,000	J 13,000	13,960	26,000	400	1

SPENT CAUSTIC from LIQUID TREATING

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R3-LT-01	R3-LT-01S	R3-LT-02	R3-LT-02S	R6-LT-01	R6-LT-01S	R13-LT-01	R13-LT-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	ND	25	ND	13	ND	ND	ND	ND	NA	NA	NA	2
Arsenic	7440382	26.00	23.7	5.00	5	< 0.10	0.01	< 0.10	ND	5.62	26.00	0.10	
Chromium	7440473	< 0.005	NR	< 0.005	NR	< 0.005	NR	< 0.005	NR	0.008	0.015	0.005	
Cobalt	7440484	< 0.25	12.3	< 0.25	1	< 0.25	ND	< 0.25	ND	4.04	23.00	0.25	
Copper	7440508	< 0.013	NR	< 0.013	NR	< 0.013	NR	< 0.013	NR	0.025	0.087	0.013	
Iron	7439896	< 0.05	NR	< 0.05	NR	< 0.05	NR	< 0.05	NR	4.23	24.00	0.05	
Lead	7439921	0.27	NR	0.12	NR	< 0.03	NR	< 0.03	NR	0.09	0.27	0.03	
Manganese	7439965	< 0.008	NR	< 0.008	NR	< 0.008	NR	< 0.008	NR	0.009	0.016	0.008	
Mercury	7439976	0.270	ND	< 0.005	ND	< 0.005	ND	< 0.005	0.00084	0.093	0.270	0.005	
Potassium	7440097	< 2.50	NR	< 2.50	NR	< 2.50	NR	< 2.50	NR	52.06	300.00	2.50	
Selenium	7782492	0.35	NR	0.06	NR	< 0.03	NR	< 0.03	NR	0.11	0.35	0.03	
Sodium	7440235	110,000	NR	43,000	NR	12,000	NR	38,000	NR	59,333	110,000	12,000	
Thallium	7440280	< 0.05	NR	< 0.05	NR	< 0.05	NR	< 0.05	NR	0.11	0.38	0.05	
Zinc	7440666	< 0.01	B 2.8	< 0.01	B 5	0.44	0.029	< 0.01	ND	0.09	0.44	0.01	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.

2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.

J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.

E Concentration exceeds the upper calibration standard.

ND Not Detected.

NA Not Applicable.

NR Not Reported, or concentration below the method detection limit.

SULFUR COMPLEX SLUDGE

Volatile Organics – Method 8260A µg/kg

	CAS No.		R1-ME-01		R1-ME-01S		R6-ME-01		R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641		8,600		NR	<	1,250		NR	1,834	6,600	25	
Benzene	71432	<	2,500	J	360	<	1,250		ND	260	420	99	1
n-Butylbenzene	104518		7,200		1,200	J	700		ND	1,830	7,200	25	
Carbon disulfide	75150	<	2,500		NR	<	1,250		NR	120	120	120	1
Ethylbenzene	100414		9,600		3,400	J	1,100		ND	2,421	9,600	160	
Isopropylbenzene	98828		ND		810		ND		ND	NA	NA	NA	2
p-Isopropyltoluene	99876		ND	J	460		ND		ND	NA	NA	NA	2
4-Methyl-2-pentanone	108101		78,000		NR	<	1,250		NR	16,100	78,000	25	
Methylene chloride	75092	<	2,500	BJ	200	<	1,250	J	220	88	150	25	1
n-Propylbenzene	103651		6,600		1,600	<	1,250		ND	1,820	6,600	25	
Toluene	108883		13,000		5,600	J	510		ND	3,003	13,000	260	
1,2,4-Trimethylbenzene	95636		47,000		16,000	J	1,800		ND	10,062	47,000	310	
1,3,5-Trimethylbenzene	108678		16,000		5,000	J	520		ND	3,629	16,000	400	
o-Xylene	95476		16,000		6,300	<	1,250		ND	3,727	16,000	160	
m,p-Xylenes	108383 / 106423		54,000		8,600	J	1,000		ND	11,374	54,000	460	
Naphthalene	91203		34,000		8,900		2,500	J	120	7,537	34,000	25	

TCLP Volatile Organics – Methods 1311 and 8260A µg/L

	CAS No.		R1-ME-01		R1-ME-01S		R6-ME-01		R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641	B	180		NR	<	50		NR	96	180	50	
Benzene	71432	<	50		50	<	50		ND	26	26	26	1
Ethylbenzene	100414		130		NR	<	50		NR	66	130	50	
Methylene chloride	75092	<	50		NR	<	50		NR	24	24	24	1
Toluene	108883		500		NR		440		NR	218	500	50	
1,2,4-Trimethylbenzene	95636		210		NR	J	23		NR	77	210	23	
o-Xylene	95476		260		NR		210		NR	124	260	50	
m,p-Xylene	108383 / 106423		630		NR		340		NR	224	630	50	
Naphthalene	91203	<	50		NR	J	49		NR	32	49	14	1

Semivolatile Organics – Method 8270B µg/kg

	CAS No.		R1-ME-01		R1-ME-01S		R6-ME-01		R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acenaphthene	83329	J	7,800	J	19,000	<	16,500		ND	3,332	7,800	165	1
Anthracene	120127	J	5,000		NR	<	16,500		NR	2,361	5,000	165	1
Chrysene	218019	<	8,800		NR	<	16,500		NR	1,383	2,600	165	1
Dibenzofuran	132649	<	8,600		NR	<	16,500		NR	1,033	1,900	165	1
Fluorene	86737	J	8,700		NR	<	16,500		NR	5,166	8,700	165	1
Isophorone	78591	J	6,700		NR	<	16,500		NR	3,166	6,700	600	1
2-Methylchrysene	3351324	<	13,200		NR	<	33,000		NR	665	1,400	330	1
1-Methylnaphthalene	90120		39,000	J	100,000	<	33,000		ND	25,666	39,000	330	
2-Methylnaphthalene	91576		58,000		180,000	<	16,500		ND	38,206	87,000	530	
Naphthalene	91203	J	13,000	J	32,000	<	16,500		ND	9,946	18,000	165	
Phenanthrene	85018		27,000	J	78,000	<	16,500		ND	12,276	27,000	580	
Pyrene	129000	J	6,500	J	19,000	<	16,500		ND	3,491	6,500	165	1

SULFUR COMPLEX SLUDGE

TCLP Semivolatile Organics – Methods 1311 and 8270B µg/L

	CAS No.		R1-ME-01		R1-ME-01S		R6-ME-01	R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Benzo(a)pyrene	50328	JB	18		NR	<	50	NR	18	18	18	1
Bis(2-ethylhexyl) phthalate	117817	J	88		NR	J	98	NR	66	98	50	
Di-n-butyl phthalate	84742	<	50		NR	JB	12	NR	40	74	12	
1-Methylnaphthalene	90120	J	78		NR	<	100	NR	39	78	18	1
2-Methylnaphthalene	91576	J	94		NR	<	50	NR	54	94	17	
3/4-Methylphenol (total)	NA	<	50	J	6.9	<	50	ND	53	66	50	
Naphthalene	91203	J	93		NR	<	50	NR	57	93	42	
Phenanthrene	85018	J	12		NR	<	50	NR	12	12	12	1
Phenol	108952	<	50		NR	<	50	NR	74	170	50	

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.		R1-ME-01	R1-ME-01S		R6-ME-01	R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905		230.0	441	<	20.0	22.2	876.0	3,600.0	20.0	
Antimony	7440360	<	6.0	ND		14.0	10	13.4	35.0	6.0	
Arsenic	7440382		33.0	58.5		17.0	17.6	34.4	120.0	1.0	
Barium	7440393		ND	10.1		ND	1.2	NA	NA	NA	2
Cadmium	7440439		1.1	NR	<	0.5	NR	1.2	3.3	0.5	
Calcium	7440702		7,700.0	NR	<	500.0	NR	6,040.0	14,000.0	500.0	
Chromium	7440473		270.0	442		18.0	13.5	245.6	900.0	18.0	
Cobalt	7440484		11.0	12.1	<	5.0	2.9	16.8	39.0	5.0	
Copper	7440508		87.0	111		81.0	62.4	96.0	150.0	78.0	
Iron	7439896		170,000.0	NR		28,000.0	NR	105,600.0	220,000.0	28,000.0	
Lead	7439921	<	0.3	NR	<	0.3	NR	1.0	2.7	0.3	
Magnesium	7439954		2,300.0	NR	<	500.0	NR	860.0	2,300.0	500.0	
Manganese	7439965		1,600.0	2550		270.0	194	846.0	1,600.0	180.0	
Molybdenum	7439987		19.0	24.5	<	6.5	4.6	21.6	64.0	6.5	
Nickel	7440020		60.0	79.3		60.0	46.3	225.6	750.0	19.0	
Selenium	7782492		140.0	213		9.5	9.1	270.3	1,200.0	0.5	
Sodium	7440235		51,000.0	NR	<	500.0	NR	15,700.0	61,000.0	500.0	
Vanadium	7440622		38.0	11.6	<	5.0	ND	14.6	38.0	5.0	
Zinc	7440666		39.0	47.3		35.0	24.4	37.2	88.0	10.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.		R1-ME-01	R1-ME-01S		R6-ME-01	R6-ME-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Arsenic	7440382	<	0.05	NR		0.49	NR	0.14	0.49	0.05	
Barium	7440393	<	1.00	0.11		2.70	0.86	1.34	2.70	1.00	
Calcium	7440439		51.00	NR	<	25.00	NR	132.20	400.00	25.00	
Chromium	7440473	<	0.05	0.13		0.12	0.12	0.06	0.12	0.05	
Cobalt	7440484	<	0.25	NR	<	0.25	NR	0.38	0.91	0.25	
Copper	7440508	<	0.13	NR		0.41	NR	0.18	0.41	0.13	
Iron	7439896		260.00	NR		570.00	NR	298.00	570.00	130.00	
Lead	7439921	<	0.02	ND		1.10	0.053	0.25	1.10	0.02	
Manganese	7439965		36.00	NR		11.00	NR	13.42	36.00	2.00	
Nickel	7440020	<	0.20	NR		2.50	NR	2.00	5.90	0.20	
Selenium	7782492	<	0.03	NR	<	0.03	NR	0.04	0.12	0.03	
Zinc	7440666	<	0.10	NR		2.40	NR	1.00	2.40	0.10	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with AP data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

CLAUS CATALYST from SULFUR COMPLEX

Volatile Organics – Method 8260A $\mu g/kg$

	CAS No.		R1-SC-01		R1-SC-01S		R4-SC-01		R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641		2,500		ND		100		79	873	2,500	20	
Acetonitrile	75058	<	625		NR		21		NR	21	21	20	1
Benzene	71432		ND	J	220		ND	J	2.3	NA	NA	NA	2
tert-Butylbenzene	98066		ND	J	130		ND		ND	NA	NA	NA	2
Carbon disulfide	75150		ND		ND		ND	J	2.2	NA	NA	NA	2
Ethylbenzene	100414		ND	J	210		ND		ND	NA	NA	NA	2
n-Propybenzene	103651		ND	J	100		ND		ND	NA	NA	NA	2
Toluene	108883	<	625		1,100	<	5	J	4.8	93	180	5	1
1,2,4-Trimethylbenzene	95636		2,600		810	<	5		ND	875	2,600	5	
1,3,5-Trimethylbenzene	108676		ND	J	310		ND		ND	NA	NA	NA	2
Methylene chloride	75092		ND	BJ	280		ND	B	5.5	NA	NA	NA	2
Methyl ethyl ketone	78933		1,400		NR		38		NR	466	1,400	20	
Naphthalene	91203		17,000		7,700	<	5	J	1.3	5,675	17,000	5	
o-Xylene	95476		ND	J	350		ND	J	1.7	NA	NA	NA	2
m,p-Xylenes	108383 / 106423		ND	J	490		ND	J	1.6	NA	NA	NA	2

TCLP Volatile Organics – Methods 1311 and 8260A $\mu g/L$

	CAS No.		R1-SC-01		R1-SC-01S		R4-SC-01		R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Acetone	67641		640		NR	<	50		NR	313	840	50	
Acetonitrile	75058	<	50		NR		100		NR	67	100	50	
Benzene	71432		ND		ND		ND	J	10	NA	NA	NA	2
Methylene chloride	75092	<	50		NR	<	50		NR	77	130	50	
Naphthalene	91203		160		NR	<	50		NR	67	160	50	

Semivolatile Organics – Method 8270B $\mu g/kg$

	CAS No.		R1-SC-01		R1-SC-01S		R4-SC-01		R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Di-n-butyl phthalate	84742	<	330		NR	<	165		NR	235	330	165	
2-Methylnaphthalene	91576	J	240	J	710	<	165		ND	190	240	165	
Naphthalene	91203		4,200		8,400	<	165		ND	1,510	4,200	165	
1-Methynaphthalene	90120	J	200	J	440	<	330		ND	200	200	200	1
Chrysene	218019	J	68		NR	<	165		NR	68	68	68	1
Fluoranthene	206440		1,000	J	2,300		480		550	548	1,000	165	
Phenanthrene	85018		2,800		5,000		670		790	1,212	2,800	165	
Pyrene	129000	J	500	J	610	<	165		ND	277	500	165	

TCLP Semivolatile Organics – Methods 1311 and 8270B $\mu g/L$

	CAS No.		R1-SC-01		R1-SC-01S		R4-SC-01		R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Bis (2-ethylhexyl)phthalate	117817		960		NR	J	16		NR	359	960	16	
Di-n-butyl phthalate	84742	<	50		NR	<	50		NR	12	12	12	1
Naphthalene	91203	J	86		NR	<	50		NR	62	86	50	
Phenol	108952	<	50		NR	<	50		NR	14	14	14	1

CLAUS CATALYST from SULFUR COMPLEX

Total Metals – Methods 6010, 7060, 7421, 7470, 7471, and 7841 mg/kg

	CAS No.	R1-SC-01	R1-SC-01S	R4-SC-01	R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	150,000	61,500	260,000	78,200	180,000.0	260,000.0	130,000.0	
Arsenic	7440382	13.0	NR	< 5.0	NR	9.3	13.0	5.0	
Beryllium	7440417	1.3	0.6	< 1.0	0.58	0.9	1.3	0.5	
Calcium	7440702	< 500.0	NR	22,000.0	NR	7,666.7	22,000.0	500.0	
Iron	7439896	130.0	NR	71.0	NR	140.3	220.0	71.0	
Manganese	7439965	ND	7.3	ND	38	NA	NA	NA	2
Selenium	7782492	< 0.5	NR	< 2.5	NR	1.1	1.7	0.5	1
Sodium	7440235	2,400.0	NR	< 1,000.0	NR	1,700.0	2,400.0	1,000.0	
Zinc	7440666	25.0	16.2	51.0	23.2	28.7	51.0	10.0	

TCLP Metals – Methods 1311, 6010, 7060, 7421, 7470, 7471, and 7841 mg/L

	CAS No.	R1-SC-01	R1-SC-01S	R4-SC-01	R4-SC-01S	Average Conc	Maximum Conc	Minimum Conc	Comments
Aluminum	7429905	18.00	NR	110.00	NR	58.67	110.00	18.0	
Barium	7440393	ND	0.027	ND	ND	NA	NA	NA	2
Calcium	7440702	< 25.00	NR	640.00	NR	230.00	640.00	25.0	
Iron	7439896	1.80	NR	5.70	NR	4.67	6.50	1.8	
Manganese	7439965	0.18	NR	0.38	NR	0.28	0.38	0.2	
Zinc	7440666	0.42	NR	0.63	NR	0.38	0.63	0.1	

Comments:

1 Detection limits greater than the highest detected concentration are excluded from the calculations.
2 Analyte not detected with EPA data, but reported with API data.

Notes:

B Analyte also detected in the associated method blank.
J Compound's concentration is estimated. Mass spectral data indicate the presence of a compound that meets the identification criteria for which the result is less than the laboratory detection limit, but greater than zero.
ND Not Detected.
NA Not Applicable.
NR Not Reported, or concentration below the method detection limit.

APPENDIX C

Summary of Runon/Runoff Information for

Crude Oil and CSO Sediments

Runon/Runoff Controls for Land Treatment Units

Crude Oil Tank Bottom Sludge (18 onsite LTUs)

Severity of the storm event that the unit's runon/runoff control system is designed to protect against:

25 yr	50 yr	100 yr	No response
6	1	8	3

Type of runon/runoff control system in place (more than one may apply):

Berms to prevent water running onto the unit	10
Berms to prevent water running off the unit	10
Berms to prevent flood water from reaching the unit	2
Dikes to prevent water running onto the unit	6
Dikes to prevent water running off the unit	7
Dikes to prevent flood water from reaching the unit	4
Diversion ditches to prevent water running onto the unit	2
Diversion ditches to prevent water running off the unit	3
Diversion ditches to prevent flood water from reaching the unit	0

Where is runoff sent:

Onsite WWTP	11
Offsite WWTP	1
Evaporation Pond	1
No runoff	2
No response	3

Stormwater control

- 16 say that contact with stormwater is possible; 2 say it is not possible. These One facility says that contact is not possible due to a 3 foot berm around the unit. One facility says that contact is not possible due to dikes around the unit which routes stormwater to the wastewater treatment plant. This facility also did not respond to the remainder of the questions in the table, accounting for most of the "no responses" that follow.

- 9 of 18 manage their stormwater under a permit.

- 13 are not in floodplains, 1 is in a 500 year floodplain, 1 is in a 400 year floodplain, 2 are in a 100 year floodplain, and 1 did not respond to this question.

Distance to nearest downgradient waterbody:

< 1/4 mile	6
1/4-1/2 mile	4
1/2-3/4 mile	2
3/4-1 mile	1
> 1 mile	3
No response:	2

Water body names and details on surface water monitoring (e.g., data, reason for monitoring) are provided, but are not included in this report.

Features affecting movement of surface water between unit and water body: 15 have such features, 2 do not, 1 provided no response.

CSO Sludge (9 onsite LTUs)

Severity of the storm event that the unit's runon/runoff control system is designed to protect against:

25 yr	50 yr	100 yr	No response
3	1	4	1

Type of runon/runoff control system in place (more than one may apply):

Berms to prevent water running onto the unit	6
Berms to prevent water running off the unit	6
Berms to prevent flood water from reaching the unit	1
Dikes to prevent water running onto the unit	2
Dikes to prevent water running off the unit	3
Dikes to prevent flood water from reaching the unit	2
Diversion ditches to prevent water running onto the unit	1
Diversion ditches to prevent water running off the unit	1
Diversion ditches to prevent flood water from reaching the unit	0
No response	1

Where is runoff sent:

Onsite WWTP	5
Offsite WWTP	1
Evaporation Pond	1
No runoff	1
No response	1

Stormwater control

- All 9 say that contact with stormwater is possible.
- 5 of 9 manage their stormwater under a permit.
- 7 are not in floodplains, 1 is in a 500 year floodplain, and 1 is in a 100 year floodplain.

Distance to nearest downgradient waterbody:

< 1/4 mile	2
1/4-1/2 mile	3
1/2-3/4 mile	1
3/4-1 mile	2
> 1 mile	1

Water body names and details on surface water monitoring (e.g., data, reason for monitoring) are provided, but are not provided in this report.

Features affecting movement of surface water between unit and water body: 8 have such features, 1 does not.